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Interaction Of Organic Solvents With A Subbituminous Coal Below Pyrolysis Temperature

Gary Paul Dorighi
(M.S. Thesis)

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Lawrence Berkeley Laboratory University of California/Berkeley

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INTERACTION OF ORGANIC SOLVENTS WITH A SUBBITUMINOUS COAL BELOW PYROLYSIS TEMPERATURE

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ABSTRACT

The interactions of a subbituminous coal with pyridine, quinoline, piperidine, ethylenediamine, and tetrahydrofuran have been studied at temperatures ranging from 100 to 350°C under the conditions of constant temperature contacting with pure solvent. The yields of extracted material were as high as 64.3 wt% with ethylenediamine at 250°C on a dry, ash-free basis. The hydrogen to carbon molecular ratios were found to be less than half that of the coal (1.01) in cases of large extracted yields. The extracted materials were generally only slightly soluble in cyclohexane or benzene, that is they consisted largely of preasphaltenes. Proton nuclear magnetic resonance studies indicated the hydrogen content of the extracted material was overwhelmingly (avg. = 88%) aliphatic. The more effective solvents were retained to a high degree in the extracted material. This fact, coupled with a hydrogen deficiency in the extract plus coal residue, suggests the formation of combinations between elements in the coal structure and solvent, accompanied by elimination of water.

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I. INTRODUCTION

Coal is certainly one of the largest potential energy resources in the United States. As our reserves of oil and natural gas diminish, more attention is being focused upon coal as an alternative source of energy as well as gaseous and liquid fuels. The essence of coal liquefaction is to convert coal to a synthetic crude oil, a fuel oil, or even gasoline-range hydrocarbons. In such conversions, the interaction of coal with an organic liquid solvent represents a central part of the process. The function of this work has been to study these interactions and to characterize the products which result.

A. Coal Liquefaction

There are a number of basic approaches to coal liquefaction, but the primary step involves bringing the coal into contact with a liquid solvent. The products of this coal/solvent contacting consist of the coal derived organic liquid, unreacted coal, mineral matter, and the contacting solvent. This step is usually followed by solids separation, solvent recovery, and further treatment of the liquid products. These latter steps mainly represent processing details, and liquefaction processes are sometimes divided into three basic categories by the nature of the primary step.

One approach is simple pyrolysis of the coal. In fact some degree of pyrolysis is involved in each of the three categories. Pyrolysis is often conducted in a high-boiling organic liquid that serves as a support medium while providing heat transfer to the coal. This is usually performed at 400°C or above. The action is primarily

thermal, and the organic liquid medium is generally recoverable from the solution essentially unchanged.

Coal pyrolysis may also be accomplished in a chemically reactive solvent. Contacting temperatures are again in the neighborhood of 400°C. In this case, the high temperatures act to thermally decompose the coal into smaller, active fragments with which the solvent may then react. Quantitative recovery of unaltered solvent is usually not possible under these conditions.

The final category combines the use of pyrolysis temperatures, chemically reactive solvents, hydrogen gas, and a hydrogenation catalyst. The reactive solvent molecules transfer hydrogen to the active coal fragments formed during pyrolysis. Hydrogen gas, with the aid of the hydrogenation catalyst, replenishes the hydrogen in the depleted solvent molecule. Molecular hydrogen, however, may also hydrogenate the active coal fragments directly. There are a number of catalysts under consideration, and both homogeneous and heterogeneous types are being proposed. The degree of recovery of both solvent and catalyst would vary with each individual process.

The interaction of coal with an organic liquid is fundamental in each approach to coal liquefaction. These liquids may act to dissolve or decompose the coal, provide a medium for catalytic hydrogenation, or themselves serve as a hydrogen transfer agent. Regardless of their use, a more complete understanding of coal/solvent interactions is vital for further development of coal liquefaction processes.

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B. Previous Work

The investigation of the interaction of coal with various organic liquids dates back to well before the beginning of this century. Early studies were preoccupied with isolating an organic substance from the coal called the "coking principle." It was believed that this substance could be added to a poor coking coal in order to increase its coking properties. These attempts failed, but they provided the starting point for further investigation of coal interactions with a broad range of organic liquids.

Solvent extraction has since been used extensively in the study of coal structure and the chemical characterization of coal. Many investigations have been concerned with the dissolution of coal, where the primary interest is in the amount and character of the dissolved (or extracted) material. Recent studies are considerably more fundamental. The prevailing attitude of investigators often seems to favor simply compiling as much information as possible concerning coal/solvent interactions.

Oele and co-workers, in 1951, divided organic solvents into the categories of non-specific, degrading, reactive, and specific with respect to their action on coal.[1] This classification is simple and provides a convenient method to review previous investigations concerning coal/solvent interactions. For a broader view of the topic, or supplementary information, the reader is referred to works by Dryden, van Krevelen, or Kiebler.[2-5]

Non-specific solvents are characterized principally by their inability to dissolve a significant amount of material from coal.

Dryden examined a number of different solvents in 1951 and found the solvents in this category to consist largely of low-boiling hydrocarbons such as benzene, ethanol, and acetone.[6] Degrading solvents provide a medium in which high temperatures (near 400°C) break chemical bonds to form smaller, soluble fragments. High-boiling, aromatic hydrocarbons such as phenanthrene are typical degrading solvents. Reactive solvents interact chemically with coal and have generally been used at temperatures ranging from 350 to 400°C. They are most often hydrogen-donor solvents, tetralin being the classic example. Specific solvents are distinguished by the property of being able to dissolve an appreciable amount of coal at temperatures below their normal boiling point. Pyridine is a typical example.

Non-specific solvents such as benzene dissolve only a small fraction of the original coal, a fraction that is believed not to form a major part of the coal structure. In 1934, Asbury reported an acute dependence of yield (fraction of original coal dissolved) on extraction temperature, when contacting a high rank, bituminous coal with benzene.[7] A recent investigation by Draemel demonstrated a weak dependence of benzene extractability on a temperature for a low rank, subbituminous coal.[8] Both investigators used pressurized, Soxhlet-type extraction devices.

Asbury reported no significant effect of particle size on the yield of benzene extractable material unless the particle were ground to micron (10^{-3} mm) size.[7] However, even under the most favorable conditions, only 30% of the original coal was dissolved after exhaustive extraction at temperatures from 220 to 260°C.

In 1970, Vahrman used non-specific solvents at low extraction temperatures to demonstrate that significantly larger amounts of aromatic and aliphatic hydrocarbons than generally expected are available from bituminous coal.[9] He proposed that these molecules are obtainable from within the micropore structure. The slit-like shape of the micropores allows flat molecules, such as benzene, to penetrate and extract these lower molecular weight species.

Degrading solvents, such as phenanthrene, generally allow dissolution of large fractions of coal at the high temperatures at which they are used. In 1951, Orchin, et al. dissolved over 90% of a bituminous coal with phenanthrene near 350°C.[10] Since the solvent was quantitatively recoverable in high purity, it was concluded that the solvent merely acted as a vehicle for thermal cracking of the coal into smaller, more soluble species. Heredy and Fugassi disputed this point in 1966 and showed, via labelled phenanthrene, that hydrogen exchange occurred between the coal and the phenanthrene.[11] They postulated that a reaction was taking place between phenanthrene and the free radicals resulting from thermal degradation of the coal.

Golumbic and co-workers correlated the fraction of original coal dissolved with the boiling point (temperature of extraction) of several degrading-type solvents.[12] The plot shows a definite increase in yield with increasing temperature. A sharp increase in yield near coal pyrolysis temperatures supports the argument that this type of solvent acts as a medium for thermal degradation into smaller, more soluble molecules.

For reactive solvents, probably the most thoroughly investigated is tetralin. Pott and Broche, in 1933, determined the optimum conditions for bituminous coal dissolution with tetralin by successive extraction at increasing temperatures.[13] They found that by increasing the temperature of extraction incrementally from 320 to 380°C, and finally to 390°C, a total yield of 64.3% could be attained. In 1936, Asbury studied the dependence of yield on temperature with tetralin in a pressurized, Soxhlet-type extractor.[14] He obtained the highest yield at an extraction temperature of 400°C.

Orchin and Storch investigated the action of a number of different solvents on a bituminous coal in 1948.[15] Their results show that a hydroaromatic with a phenolic group, such as o-cyclohexylphenol, is even more effective in dissolving coal than tetralin at 400°C.

Wise recently reviewed an interesting technique for checking the activity of various organic compounds with respect to coal.[16] A concentration of about 5% of the compound in recycled, spent,. degrading solvent was interacted with the coal. If the subsequent yield were higher than that of the degrading (tar-oil) solvent alone, the substance was referred to as a "tar-oil activator." The experiments indicated that the hydroaromatic analogue was always more active than the corresponding aromatic. For example piperidine was more effective than pyridine as a tar-oil activator. This evidence points out the hydrogen-donor capability of hydroaromatics.

The role of hydrogen transfer in the mechanism of coal dissolution by tetralin has been the subject of much debate. In 1966, Hill proposed a two step mechanism for dissolving coal with tetralin which essentially

ignores hydrogen transfer.[17,18] The first step is a diffusion-controlled reaction where "dissolving out of included materials" occurs from within the micropore structure. The second step is a chemically-controlled dissolution of the coal structure. Hydrogen transfer reactions are regarded as a second order process at temperatures from 350 to 450°C.

Curran, et al. proposed, in 1967, that hydrogen transfer occurs from the solvent molecules (tetralin, or other hydrogen donors) to the thermally-formed free radicals in the coal structure.[19] Thermal decomposition to form free radicals was suggested as the rate-determining step. This agrees with the results of experiments conducted by Draemel in 1975.[8] In his study of the effect of temperature on tetralin extraction of a subbituminous coal, there was no evidence of hydrogen transfer below the pyrolysis (320°C) temperature. The mechanism of free-radical formation at pyrolysis temperatures followed by hydrogen transfer from a suitable solvent is also supported by Wiser.[20,21]

It had been observed that material extracted from coal with a hydrogen-donor solvent is of relatively low molecular weight and soluble in mild solvents such as benzene.[22] A few years later, in 1976, Neavel confirmed this observation.[23] He explained the phenomenon in terms of the ability of the hydrogen-donor to stabilize the thermally generated free radicals by adding hydrogen to form low molecular weight species. Conversely, treatment of coal by a non-donor solvent produces more benzene insoluble material. This is probably due to recombination of free radicals to yield molecules of high molecular weight.

Particle size is not generally believed to be a significant factor in the dissolution of coal by chemically reactive solvents.[19,24] Guin and co-workers reaffirm that particle size is of little importance, because of the rapid disintegration of coal particles in these high temperature extractions.[25]

Dryden defined specific solvents as those which could swell a low rank coal and extract a considerable amount of material from it at room temperature.[6] They typically consist of a molecule with an oxygen or a nitrogen atom possessing an unshared pair of electrons. One common example is pyridine. The relationship of solvent power with respect to coal and the availability of this electron pair was studied by Halleux and Tschamler, in 1959, for a number of pyridine-type bases.[26] Their studies conclude that solvent power generally increased with increasing basicity, unless steric interaction became a major factor between the organic base and substituents surrounding the acid sites in coal.

Many attempts have been made to correlate solvent activity with physical properties such as surface tension, internal pressure, dielectric constant, and dipole moment.[27,28,29] Dryden showed that these attempts largely fail over the broad range of solvents examined in his investigation.[6]

An extensive amount of work was done by Dryden in 1951, exploring the action of a number of specific solvents on coals of various rank.[30] The results demonstrate a maximum of solvent power for pyridine in the intermediate rank coals. The action of ethylenediamine and monoethanolamine, however, increased as the carbon content of the coal decreased. In 1960, Dormans and van Krevelen studied the action of pyridine on coals

of different rank at tempertures up to pyridine's normal boiling point of 115°C.[31] Their results indicated that maximum solubility in pyridine occurred for coals having a carbon content of 87 percent. This is in general agreement with the findings of Dryden.[30]

In an effort to predict the action of specific solvents on coals of different rank, van Krevelen has utilized Flory's theory of polyfunctional condensation to calculate solubility parameters for a number of coals.[32] The solubility of a coal in a particular solvent is predicted by taking the square of the difference between the solubility parameter of the coal and the solvent. If the result is less than (or equal to) one, the solubility of the coal in that particular solvent is high. The solubility parameters predicted for coals of different rank by van Krevelen correctly describe the increased solvent power of ethylenediamine and monoethanolamine toward lower rank coals. Sanada and Honda have continued this work, in 1966, by studying the relationship between the degree of equilibrium swelling and the solubility parameter for coals of different rank.[33] Kirov and co-workers have compared the solubility parameters predicted by van Krevelen's method with those determined experimentally for a medium rank coal (82 percent carbon) and its solvent extract.[34] Solubility parameters were also determined for the extraction residues of three coals of different rank. These values did not increase with decreasing rank (as predicted by van Krevelen's method), but remained essentially constant.

The nature of the extracted material as a function of extraction conditions was studied extensively by Dryden.[35,30] The yield of extract was greater for solvents with high boiling points due to the high

temperature of extraction. Varying the size of the coal particles produced no significant effect on the amount of extracted coal. Molecular weight measurements were taken of the coal extracts, although Dryden offers evidence for the colloidal nature of solutions for both ethylenediamine and pyridine extracts.[35] These findings are not in agreement with those of Wynne-Jones, Blayden, and Shaw, in 1952.[36] Their results describe average molecular weights for pyridine extracts by osmometry and ultracentrifugation which are far too low for such solutions to be colloidal. This view was later supported by Sakabe by measurement of the diffusion coefficient of pyridine extract in solution by a porous diaphragm method.[37]

The action of various solvents on coals of different rank has been studied extensively by numerous investigators. The role of non-specific solvents is considered to be minor, because of their failure to attack the basic coal structure. Degrading solvents act only at very high temperatures and alone are not suitable for coal liquefaction processes. The reactive solvent system has been thoroughly investigated; however, a better understanding of the mechanism of hydrogen transfer from the solvent to the coal is essential. The need for hydrogen to replenish that which is donated by the solvent and the required high temperatures also are disadvantages of this approach. Specific solvents have been found to dissolve a significant amount of coal at temperatures below their normal boiling point. However, these investigations have been confined to intermediate and high rank coals. The extension of this type of study to coals of lower rank, along with further characterization of the material extracted from the coal,

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is necessary for a better understanding of coal/solvent interactions below pyrolysis temperature.

C. Scope

Previous investigations have largely ignored the action of organic solvents on subbituminous coals. Studies involving specific solvents have been conducted at temperatures near or below the normal boiling point of the solvent. The subject of investigation in this study is the interaction of a subbituminous coal with specific solvents at temperatures up to the point of coal pyrolysis, which is often above the normal boiling points of the solvents involved.

The single coal used for this investigation is a western, low-sulfur, subbituminous coal. The solvents under consideration may be classified as specific; that is, the solvent molecules contain either an oxygen or a nitrogen atom possessing an unshared pair of electrons. The interaction of these solvents with the coal is studied for temperatures from 100 to 350°C. This range contains both the normal boiling points of most solvents and the pyrolysis temperature of the subbituminous coal.

This investigation includes determination of the dependence of yield on the temperature and duration of coal/solvent contacting. It also examines the nature of the extraction products by characterizing both the extracted material and the remaining coal residue.

D. Nature of Results

The approach of this investigation was to treat a subbituminous coal with selected specific solvents at controlled temperatures under conditions where extracted material was removed from contact with

the coal. The usual contacting time was 4 hr, and temperatures ranged from 100 to 350°C. The solvents used for contacting were pyridine, monoethanolamine, ethylenediamine, quinoline, piperidine, and tetrahydrofuran.

The solubility of the coal varied widely with the solvent and temperature of extraction. Values range from 7.4% using tetrahydrofuran at 150°C to 64.3 % using ethylenediamine at 250°C on a dry, ash-free basis. The nature of the extracted material, as determined by the molecular hydrogen to carbon ratio, also changed significantly with solvent and extraction temperature. This ratio varied from 0.430 with ethylenediamine at 150°C to 1.51 with tetrahydrofuran at 150°C. The value for the untreated coal is 1.01. The coal/solvent extracts displayed limited solubility in mild solvents, such as cyclohexane and benzene, but were readily soluble in pyridine.

The results of this investigation demonstrate that specific solvents may dissolve considerable amounts of low rank coal at relatively moderate conditions. However, much of the dissolved material was of very high molecular weight; and a high yield was often accompanied by a high degree of solvent incorporation in the extracted material.

II. EXPERIMENTAL STUDIES

For the purpose of this investigation, it is necessary to conduct coal/solvent contacting at controlled temperatures ranging from 100 to 350°C. Duration of contacting should be sufficient to provide a satisfactory approach to equilibrium dissolution without requiring impractically long times for execution of experiments.

Coal/solvent contacting should take place without further interaction between the coal and previously dissolved material. In short, the apparatus for this investigation must provide precise temperature control over a broad range, be able to operate for extended periods of time without attendance, and avoid interactions between the coal and the already extracted material.

Both a stirred batch autoclave and a mechanically agitated sealed tube fulfill the first two requirements in addition to providing the intimate coal/solvent contacting desired. However, unless the solution of extracted material is sufficiently dilute, there exists the possibility of further interaction of some dissolved material with remaining coal.

An extraction device, where pure solvent is vaporized from a solution of extracted material, condensed above the coal, and drained continuously over the coal, satisfies all of the required conditions. Such a device is called a Soxhlet-type extractor and may be operated under controlled pressure in order to boil the mixture at other than its atmospheric boiling point.[8] A pressure-controlled, Soxhlet-type extractor was used for this investigation.

Dryden observed little difference between the results of sealed tube extraction and exhaustive Soxhlet extraction at the same

temperature.[30] At the elevated temperatures to be examined in this study, however, significant interactions between coal and dissolved material may occur that would not take place in Dryden's lower temperature experiments. A pressurized Soxhlet-type device also offers a responsive and easy-to-control system of maintaining constant temperature by varying the pressure of an inert gas above the boiling liquid.

A. Apparatus

The pressure-controlled, Soxhlet-type extractor used in this investigation was described by Draemel and is depicted in Fig. 1.[8] Solvent is vaporized from the solution of extracted material and condensed above the Soxhlet cup in the condenser. The solvent flows continuously from the condenser into the Soxhlet cup, where the coal is contained in a 200 mesh stainless steel wire basket with a close fitting top. When the Soxhlet cup fills to the overflow level, the solvent and extracted material are siphoned into the solvent vessel. A 4-liter surge vessel acts to damp short duration fluctuations in pressure occurring when the inert gas is either vented or added to the apparatus. A temperature recorder displays the input from thermocouples in the solvent vessel, Soxhlet cup, condenser inlet, condenser outlet, and at the bottom of the 4-liter surge vessel. Temperature may be controlled automatically by controlling pressure with a pneumatic control valve and a recording pressure controller. The system may be operated under positive or negative pressure, giving one the flexibility to extract above or below the atmospheric boiling point of the solvent.

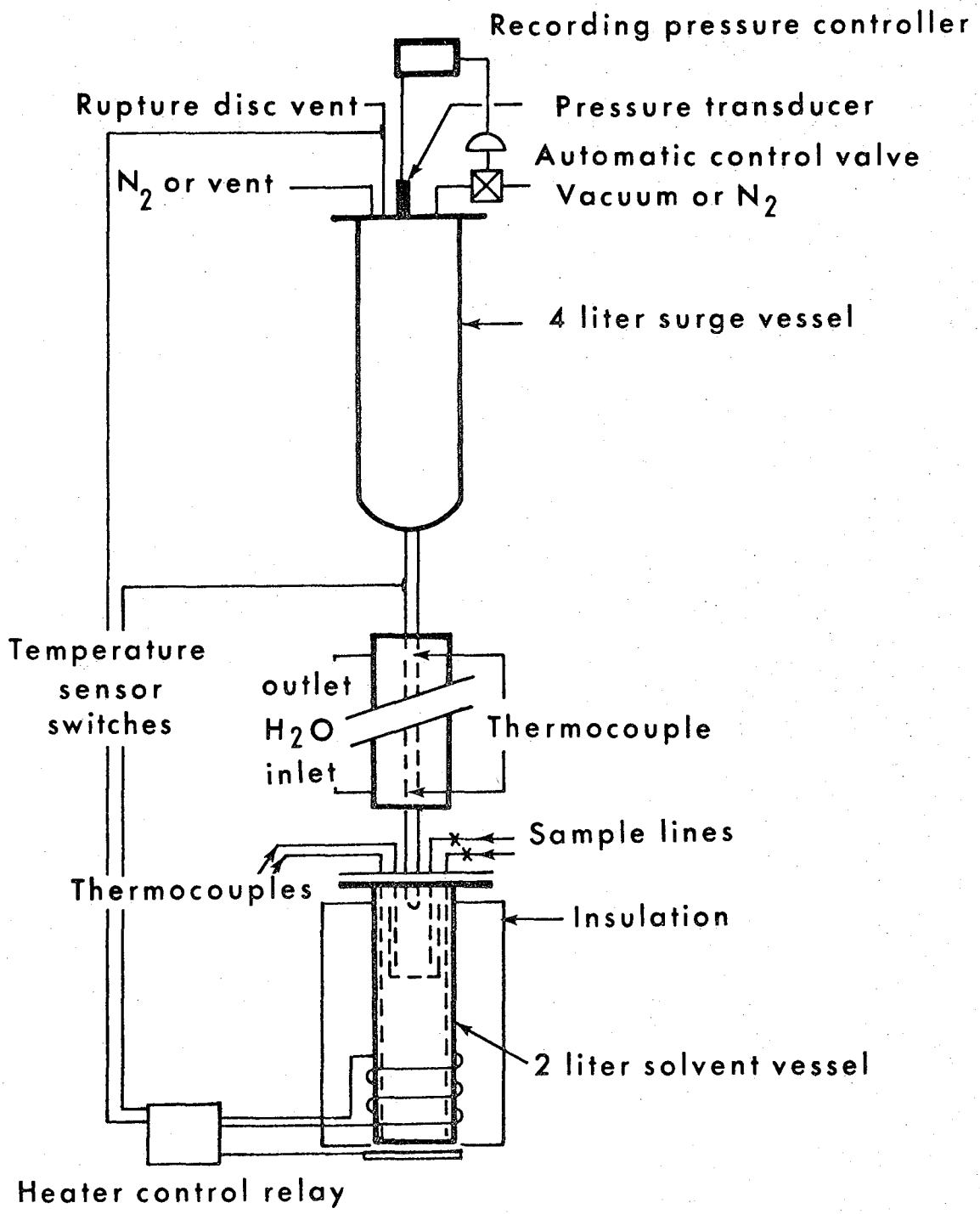

Fig. 1. High pressure coal/solvent contacting apparatus. Operating ranges: 0-500 psia, 50-370°C.

The extractor may be operated under pressures of 0 to 500 psia with temperatures ranging from 50 to 370°C.

The entire apparatus is protected by a 572 psig rupture disc and two temperature sensing switches connected to a heater control relay. In the event of rupture disc or cooling water failure, the increase in temperature would be detected at the temperature sensing switches, and the relay would shut off the heaters.

B. Materials

The coal used in this investigation was a low rank, low sulfur subbituminous coal from the Roland Seam of the Wyodak Mine in Gillette, Wyoming. It had been stored under a nitrogen atmosphere as 20-lb samples in sealed plastic bags from a previous investigation, ground to a size of minus 1/16 in.[8] One whole bag was initially sieved in order to separate the fraction that was already the desired minus 28 plus 150 (Tyler) mesh. The plus 28 mesh coal was then ball-milled until all of the sample was reduced to within the range of minus 28 plus 150 mesh. This was then riffled and stored in sealed paint cans under an atmosphere of nitrogen. As needed the total contents of each can were transferred to a desiccator and stored for use under a vacuum of about 2 mm Hg with Drierite and sulfuric acid as desiccant. The remaining fines (minus 150 mesh) represented only about 10% of the total weight of coal and were discarded.

Representative samples of the coal were submitted for analysis to both the Commercial Testing and Engineering Company in Denver, Colorado and the University of California, Berkeley, Microanalysis Laboratory.

The Commercial Testing and Engineering Company used ASTM Test D271-70 for their analyses. The Microanalysis Laboratory used a Perkin-Elmer (Model 240) Analyzer for carbon, hydrogen, and nitrogen analyses and the Grote Combustion Method for determination of sulfur, chlorine, and ash.[38] The results of these analyses are given in Tables I and II.

For this study, the most important analyses are those for carbon, hydrogen, nitrogen, and ash. The disagreement between the two laboratories in these areas is only a few percent and may be attributed to different analytical techniques. The precision for the five samples of coal submitted to the Microanalytical Laboratory was good for carbon, hydrogen, nitrogen, and ash. Since all analyses of extracted material and residue were submitted to the Microanalytical Laboratory for analysis, their values were used for the elemental analysis of the Roland Seam Coal used in this investigation.

The organic solvents used in this study were pyridine, monoethanolamine, ethylenediamine, quinoline, piperidine, and tetrahydrofuran. With the exception of tetrahydrofuran, all the solvents used were picked for their classification by the previous definition as a specific solvent. Van Krevelen's solubility parameters also indicate that monoethanolamine and ethylenediamine would be excellent solvents for a low rank coal.[32] Tetrahydrofuran was chosen because it possesses an oxygen atom with an unshared pair of electrons and is able to dissolve most material already extracted from coal by another solvent.

Table I. Analysis of Roland seam coal by the Commercial Testing and Engineering Company.

	As Received	Dry Basis
	Proximate Analysis	
% Moisture	1.00	--
% Ash	14.35	14.49
% Volatile	46.26	46.73
% Fixed Carbon	38.39	38.78
Btu	10790	10817
% Sulfur	1.03	1.04
	Ultimate Analysis	
% Moisture	1.00	
% Carbon	61.41	62.03
% Hydrogen	4.89	4.94
% Nitrogen	1.02	1.03
% Chlorine	0.07	0.07
% Sulfur	1.03	1.04
% Ash	14.35	14.49
% Oxygen (difference)	16.23	16.40
H/C Molcular Ratio	0.96	0.96

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Table II. Analysis of Roland seam coal by the University of California Berkeley, Microanalysis Laboratory.

Elemental Analysis* (Dry Basis**)	
% Carbon	59.28 ± 0.9
% Hydrogen	5.01 ± 0.02
% Nitrogen	0.97 ± 0.03
% Chlorine	0.17 ± 0.08
% Sulfur	0.46 ± 0.09
% Ash	15.34 ± 0.7
% Oxygen (difference)	18.77
H/C Molecular Ratio	1.01

* Values reported represent an average value of five samples submitted along with the standard deviation where appropriate.

** Samples were dried for 24 hours at 105°C in an oven evacuated to 250 mm Hg and swept by nitrogen.

The final acceptability of each of the solvents was based upon cost, toxicity, available purity, and anticipated activity with respect to the coal. Pyridine and tetrahydrofuran were both Mallinckrodt (A.R.) grade, while quinoline and monoethanolamine were Baker (A.R.) grade. Piperidine was supplied by Baker at 99.0% purity, and the ethylenediamine was obtained from Mallinckrodt at 98.0% purity. With the exception of tetrahydrofuran, all solvents were used directly from the bottle. Tetrahydrofuran is known to form peroxides on standing and was distilled with a packed laboratory column before use. The first 10% and the last 10% of the condensate were discarded, and the solvent was then immediately charged to the extractor.

C. Procedure

An effort was made to use exactly the same procedure for every solvent in each coal/solvent contacting experiment. This was not always possible, because new conditions and problems arose as the investigation proceeded from solvent to solvent. The procedure outlined in this section is representative, and significant deviations will be discussed here or in later sections as they come under consideration.

Approximately 20 grams of coal was removed from storage in the desiccator and washed with distilled water over a 170 (Tyler) mesh screen to further remove any fine particles. It was then dried for 24 hours at 105°C in a vacuum oven evacuated to 250 mm Hg and swept by nitrogen. Upon removal from the oven, it was quickly transferred to the tared 200 mesh stainless steel wire basket with a close fitting top, rapidly weighed, placed in the contacting cup of the extraction apparatus; and the apparatus closed. It was observed that Viton

O-rings reacted with most of the solvents, so copper gaskets (monoethanolamine, tetrahydrofuran) and aluminum gaskets (quinoline, piperidine, ethylenediamine) were used to seal the apparatus. The extractor was then evacuated to about 0.1 mm Hg for 15 min to remove air and any traces of moisture. From between 400-600 ml of solvent were then drawn into the extractor through the solvent vessel sampling line. The vacuum was then adjusted to about 250 mm Hg and maintained for 15 more minutes. The pressure was then adjusted with the inert gas to the pressure required for extraction at the desired temperature.* The cooling water was supplied to the condenser from a constant temperature water bath, which generally maintained the temperature at 25°C. The heaters were next switched on, and the extraction time was measured from the point at which the temperature in the contacting cup reached the desired temperature of extraction. Once the temperature stabilized, it could be maintained by simply operating the system "closed." The temperature did not change as long as the pressure remained constant. For long, unattended contacting, or when the system was operated under negative pressures, the pressure control system was used as outlined by Draemel.[8] This enabled temperature control to within 5°C of the desired temperature. Both the system pressure and all monitored temperatures were recorded continuously for each experiment.

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* In the later experiments involving quinoline and piperidine, the solvent was first briefly refluxed at 250 mm Hg to further degas it. Finally with tetrahydrofuran, the inert gas was bubbled through the solvent with the sample line to saturate the solvent with the gas and strip unwanted gases from the system.

The solvent reflux rate varied from 2 to 4 liters per hour. This could be checked from the temperature rise across the condenser or by counting the small fluctuations on the temperature recording that occurred every time the contacting cup emptied. Tighter control was not possible due to the inability to finely adjust the heater input to compensate for differences in the heat of vaporization and heat losses, which would vary with solvent and extraction conditions. The reflux rate would only become an important factor if it were so low that the dissolution process was equilibrium-limited. Under our conditions, however, the solution in the contacting cup was changed at least once every 3 min; and that would not be a problem.

Samples could be taken through the sample lines, while the apparatus was in operation, in order to study the variation of the amount or nature of extracted species with time. After sampling, the hold-up in the line was forced back into the system under the pressure of an inert gas.

When the experiment had proceeded for the desired amount of time, the heaters were switched off; and the pressure of the system was slightly increased to stop solvent boiling. The solvent vessel was then allowed to cool a number of hours.

For experiments where gas analysis was to be conducted, helium was used to pressurize the extractor; and no gas was vented during the extraction. Samples of the gas produced during coal/solvent contacting were taken when the entire apparatus had cooled to room temperature. It was important to prevent contamination of the gas sample with air. De-gassing of the solvent and the extraction apparatus

has already been discussed. The required apparatus for gas sampling is represented in Fig. 2. The two glass sample bulbs (300 or 500 ml) were fitted to the glass tubing manifold by standard taper ground glass joints. A 3-way valve sent the gas flow from the extraction apparatus to either the glass tubing manifold or the vent. The gas sampling apparatus (glass) was connected to the top of the 4-liter surge vessel (steel) by means of a glass socket joint fitted to a brass ball. Flow to the gas sampling apparatus was controlled by a diaphragm valve.

Both sample bulbs and the glass tubing manifold were evacuated to roughly 10^{-5} Torr by a diffusion pump prior to sampling. The 3-way valve was closed to the manifold and sample bulbs, and the apparatus was fitted to the top of the 4-liter surge vessel. The gas from the extractor was vented to the atmosphere by opening and closing the diaphragm valve. The venting was pulsed to insure a well-mixed gas sample. Once the venting was completed to atmospheric pressure, the 3-way valve was opened to the manifold; and the gas sample was collected. The stopcocks of the bulbs were closed, and the sample was ready for analysis. The sample was collected in two bulbs to insure a reserve sample in the event the first analysis failed. The concentration of each of the gaseous species in the gas mixture is accurately determined at the time of analysis. Assuming a well-mixed gas sample and ideal gas behavior, the amount of each species may be calculated from the observed pressure, volume, and temperature of the total amount of gas in the extraction apparatus at the time of sampling.

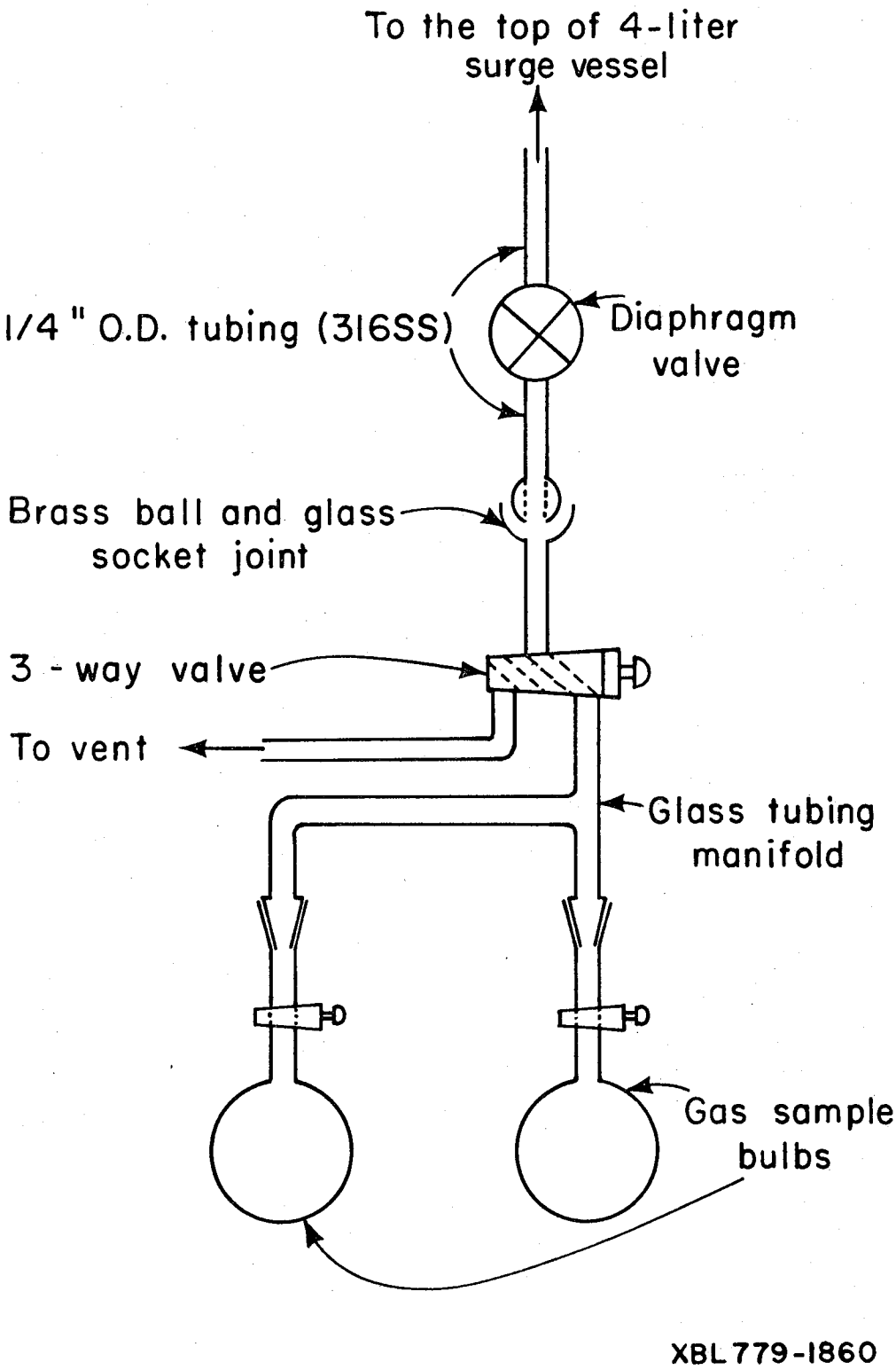


Fig. 2. Product gas sampling apparatus.

After the gas sample was taken, the extraction apparatus was dismantled. The remaining coal residue was washed from the wire basket with room temperature contacting solvent onto a tared piece of filter paper fitted inside a Buchner funnel. When the solution from the funnel entering the vacuum flask became clear, the residue was then washed with a liter of boiling water. The filter paper and residue were removed from the Buchner funnel and dried for 24 hr at 130°C (200°C for quinoline) in an oven evacuated to 250 mm Hg and swept by nitrogen. The procedure was designed in this way to: first, remove all of the extract from the residue; then, to rinse most of the solvent from the surface of the coal; and finally, to dry the coal and remove any traces of solvent from the inner structure.

The solution of extract in solvent was divided equally among 250 ml glass bottles and centrifuged for 1 hr at 2000 rpm. The supernatant liquid was then vacuum filtered, collected; and two 10 ml aliquots were pipetted into two tared petri dishes for evaporation to dryness. The total volume of recovered solution was then measured in a 1000 ml graduated cylinder. The residual material was rinsed with room temperature contacting solvent from the glass bottles onto a tared piece of filter paper fitted inside a Buchner funnel. The residue on the filter paper was washed as before first with solvent and then with water. The filter paper and residue along with the 10 ml sample in the petri dishes were dried for 24 hr at 130°C (200°C for quinoline) in an oven evacuated to 250 mm Hg and swept by nitrogen. The centrifuging and filtering steps were necessary to remove any amount (significant at times) of undissolved coal

particles which were small enough to pass through the 200 mesh wire basket. The 10 ml aliquots were chosen for evaporation, rather than the total extract solution, to insure that diffusion of the solvent to the liquid surface would not be hindered. Diffusion of the solvent through the total extract solution, which becomes much more concentrated as evaporation proceeds, would probably unacceptably limit the solvent evaporation rate from the extract.

The average weight of the dried extract in the two petri dishes determines the concentration of the extract solution (in g/ml). The total volume of recovered solution represents the total volume (in ml) of solvent in the solution. Both these values assume that any contribution to the volume by the extract is negligible. This is a good assumption at the very low concentrations encountered. The summation of the two residue weights determines the total amount of undissolved coal (in g). The yield can, therefore, be determined on the basis of the extract or residue. The extract yield is determined by multiplying the total volume of solvent by the extract concentration to give the total mass extracted. This number is then divided by the weight of the original dry or dry, ash-free coal charged to the system. The yield may be reported on a dry or dry, ash-free (daf) basis. The residue yield, on a dry basis, is simply the weight of the residue divided by the weight of the original coal charged.

At the end of each experiment, the solvent vessel, contacting cup, and wire basket were cleaned with chromic acid, rinsed with water, and then rinsed with acetone to remove any traces of tar or solvent

0 0 0 0 4 8 0 3 3 5 9

residue. The sample lines were also flushed with acetone to remove any remaining solution.

Before a new contacting solvent was introduced to the system, a "practice" or "blank" run was performed in which only solvent (no coal) was charged to the system. This blank run served to clean any remnants of the previous solvent out of the system. It also enabled the operator to study the vapor pressure characteristics of the solvent and determine whether degradation of the solvent would occur at the temperatures and time periods to be used.

D. Analyses

In order to derive the most information possible concerning coal/solvent interactions, it is necessary to study the nature of both the extracted material and the remaining, undissolved coal residue. The amount of data that could be gathered was limited to some degree by the availability of suitable analytical equipment. Some rather simple analyses, however, provided significant information.

Elemental analysis for hydrogen, carbon, and nitrogen of both the coal residue and solvent extract enabled the characterization of these two products by their molecular hydrogen to carbon ratio. This analysis also provided the necessary data to determine their extent of solvent retention and to perform mass balances over the system of original coal, undissolved coal, and dissolved material. Mass spectroscopy was used to analyze the gases produced during contacting experiments. The knowledge of both the amount and species of these gases allowed the completion of the list of products derived from coal/solvent contacting. The extracted material was

separated into three distinct fractions of oils, asphaltenes, and preasphaltenes by its respective solubility in cyclohexane, benzene, and pyridine.[39] This separation was used to measure the effectiveness of a particular contacting solvent in converting coal to the desired oil fraction. Vapor pressure osmometry was used to obtain number average molecular weights of the various extract fractions. Nuclear magnetic resonance was used to study the aliphatic/aromatic nature of the solvent extract.

1. Analysis for Hydrogen, Carbon, and Nitrogen

All values of hydrogen, carbon, and nitrogen mass fractions for coal, extract, and residue were determined by the University of California, Berkeley, Microanalysis Laboratory. The tests were performed on a Perkin-Elmer (Model 240) "CHN Analyzer." All samples were submitted in tightly-sealed vials after being dried for 24 hr at 130°C (105°C for raw coal) in an oven evacuated to 250 mm Hg and swept by nitrogen.

2. Mass Spectroscopy

For this study it was desired to determine the amount and species of gas produced during coal/solvent contacting. Since the atmosphere above the boiling liquid consisted mostly of the inert gas used to pressurize the apparatus, it was necessary to separate it first from the rest of the gases in order to provide a high enough concentration of these gases for mass spectroscopic analysis. The process outlined in this section for removing the inert gas from the rest of the sample is based upon the fact that helium will pass directly through 5 angstrom molecular sieve. Therefore, when a gas sample was desired for a

particular contacting experiment, helium was used for pressurizing the extractor.

The sample of gas collected at the end of a coal/solvent contacting experiment may be considered a three component system. The largest component is the inert gas (helium) used to pressurize the extractor. Another major component is the vapor from the contacting solvent. The smallest component consists of the gas produced during the contacting experiment. Separation of the gas mixture into these three components depends on the molecular size and boiling point of each species. The helium is vented while the solvent vapor and product gases are either condensed at the temperature of liquid nitrogen (77.4°K) or retained by 5 angstrom molecular sieves. The product gases are then collected while the solvent is condensed at the temperature of a carbon dioxide bath (195°K).

The apparatus represented in Fig. 3 was used to separate the gas sample into three fractions. The system was made from Pyrex glass and assembled on a laboratory rack for convenience. Any junctions were either glass-blown or assembled with ball and socket joints (not shown). Except for the 3-way valve, all valves are simply stopcocks. The gas buret and Toeplar pump are not shown. The vacuum sources are both diffusion pumps.

Before the contents of the sample bulb were introduced to the system, the whole apparatus was evacuated to about 10^{-5} Torr by opening all of the valves and evacuating with a diffusion pump. Valve 1 was then closed, and liquid nitrogen baths placed on Traps 1, 2, and 4. The sample was then introduced by opening the stopcock

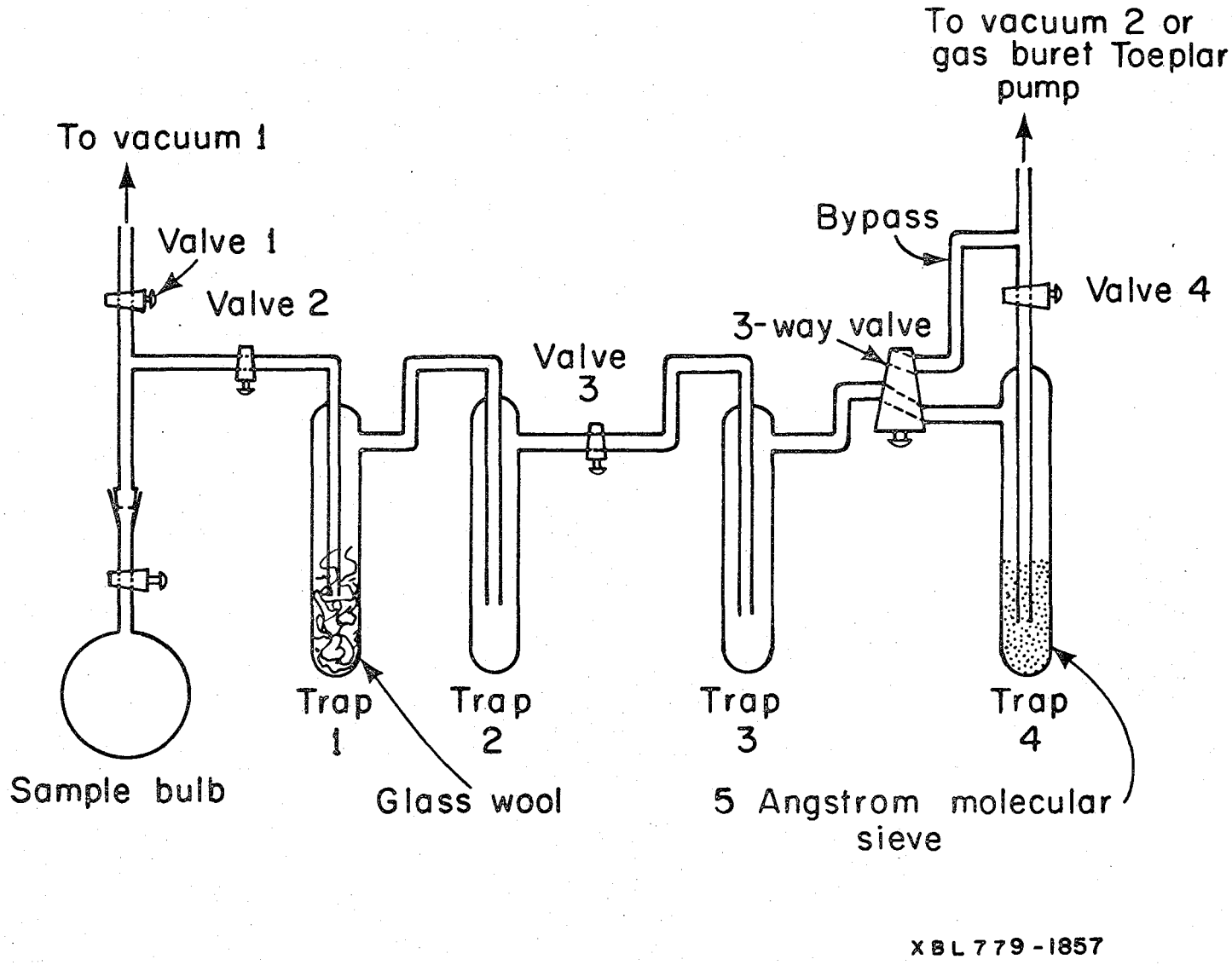


Fig. 3. Product gas separation apparatus.

on the sample bulb. All of the helium in the sample was immediately pumped out at Vacuum 2, since it is neither condensable at a temperature of 77.4°K, nor absorbed by 5 angstrom molecular sieve. Other gases such as argon, oxygen, nitrogen, carbon monoxide, methane, and hydrogen, are volatile at this temperature but were absorbed by the molecular sieve. These absorbed gases (now in Trap 4) were then isolated by closing the 3-way valve to all three lines. By heating Trap 4 to 150°C, all of the gases absorbed on the molecular sieve were evacuated by the Toeplar pump, measured in the gas buret, and collected in a separate sample bulb. This sample was called fraction I.

Since the gases which are volatile at 77.4°K (fraction I) have been removed, the remaining gases from the original sample were all contained in Traps 1, 2, or 3. The glass wool in Trap 1 was used to prevent the formation of a "fog" which would not condense on the walls of a cold trap.

The gases in the three traps were collected in a single trap (Trap 1), so that they could be separated according to their volatility at 195°K. The liquid nitrogen bath was removed from Trap 2, and Valve 2 was closed. Trap 2 and Trap 3 were then warmed to about 50°C with water in order to drive the remaining gases from the original gas sample back into Trap 1. A liquid nitrogen bath was then placed on Trap 3 and a bath of dry ice in trichloroethylene (195°K) placed on Trap 1. The 3-way valve was opened (to connect Trap 3 with Bypass); the liquid nitrogen bath removed from Trap 1; and the pumping from Vacuum 2 continued. Everything volatile at 195°K was collected in Trap 3, and the material remaining (condensed at 195°K) was retained

in Trap 2. The gases in Trap 3 were then isolated by closing Valve 3; they will be referred to as fraction II. This fraction was collected by removing the liquid nitrogen bath from Trap 3; warming Trap 3 to about 50°C; evacuating the gas with the Toeplar pump; measuring it in the gas buret; and storing it in a separate sample bulb.

The remaining gases (fraction III) were then recovered from Trap 2. The original sample bulb was replaced by a finger trap. Valve 1 was opened and the finger trap and system up to Valve 2 was evacuated by Vacuum 1 to about 10^{-5} Torr. Valve 1 was then closed and Valve 2 opened for access of fraction III to the finger trap. The dry ice/trichloroethylene bath was removed from Trap 2 and placed around the finger trap. Trap 2 was warmed to 50°C, and the remaining fraction was driven off and collected in the finger trap.

All three samples were then separately analyzed by a CEC (Model 21103A) mass spectrometer according to the method outlined by Washburn, Wileys and Rock.[40]

3. Oil, Asphaltene, Preasphaltene Separation

The material extracted from coal may be separated into various fractions according to its solubility in a particular solvent. It was decided to use the classification of oils, asphaltenes, and preasphaltenes for this study.[39] Only the oil fraction is soluble in cyclohexane. Asphaltenes are not soluble in cyclohexane but are in benzene. Preasphaltenes are soluble only in pyridine.

The literature is cluttered with different laboratory techniques for the isolation of these three fractions. In 1951, Weller, et al.

separated the benzene insolubles from the benzene solubles by exhaustive Soxhlet extraction with benzene.[41] After driving off the benzene from the benzene solubles by distillation, the concentrate was treated with five times its own weight of n-hexane. The insoluble material was called asphalt, and the material soluble in n-hexane at room temperature was referred to as oil. Recently, Sternberg defined the pyridine solubles of the benzene insolubles as preasphaltenes.[39] Currently, at the Pittsburg Energy Research Center, the benzene solubles are obtained by Soxhlet extraction near the boiling point of benzene.[42] The benzene insolubles are further extracted with pyridine to yield preasphaltenes and pyridine insolubles. The benzene solubles are concentrated to an approximate volume ratio of 1:1 benzene/solubles. The asphaltenes are then precipitated from the benzene solubles at room temperature with pentane.

In this study, the material extracted by coal/solvent contacting was Soxhlet extracted successively by cyclohexane, benzene, and pyridine (near their normal boiling points) to yield oils, asphaltenes, and preasphaltenes respectively. This method proved extremely simple and attained reproducible results.

Since the amount of material available for this analysis was usually small (less than 0.5 gram), the apparatus used was correspondingly scaled down. The double-wrapped cellulose extraction thimble (13-15 micron porosity) measured 10 mm x 50 mm, and the boiling flask contained 20 ml of solvent.

A portion of the extracted material was dried for 24 hours at 130°C in a vacuum oven evacuated to 250 mm Hg and swept by nitrogen.

The thimble was dried similarly for 3 hr at 105°C, removed from the oven, and immediately weighed before it could pick up any moisture from the air. The sample was then crushed into fine particles and transferred into the tared thimble. The thimble (with sample) was redried for 2 hr at 105°C under the same conditions to remove any moisture taken up in thimble-filling process. Upon removal from the oven, the thimble containing the sample was quickly weighed and placed into the extraction apparatus. The flask was charged with 20 ml of cyclohexane, and the sample extracted for at least 20 hr or until the refluxed solvent became clear. The thimble was removed from the extractor and dried for 4 hr at 105°C in a vacuum oven evacuated to 250 mm Hg and swept by nitrogen. It was then removed, quickly weighed; and the difference from its original weight divided by the sample weight gave the percent of oils in the original extract.

The thimble was again placed into the extraction apparatus, and the system was charged with 20 ml of benzene. After 20 hr of extraction or until the refluxed solvent became clear, the thimble was removed from the apparatus and dried again at the same conditions as after the cyclohexane extraction. It was then removed, quickly weighed; and the difference from its previous weight divided by the sample weight determined the percent of asphaltenes in the original extract.

The same procedure was repeated with pyridine as solvent to find the percent of preasphaltenes in the original sample. Anything which remained in the extraction thimble after treatment with pyridine was called pyridine insolubles.

4. Vapor Pressure Osmometry

Number average molecular weights of extracted species reported in this study were determined by a Hewlett-Packard (Model 320B) Vapor Pressure Osmometer. The fundamental component of the instrument consists of two thermistor beads connected to a null bridge circuit. The beads are contained in a chamber saturated with solvent vapor. When the two beads both have drops of pure solvent on them, the bridge is nulled. When a drop of solute in solvent is placed on one of the beads, the "distillation effect" of pure solvent vapor to that bead produces a rise in its temperature. The temperature difference between the two beads is measured as a voltage difference on the null bridge.

The procedures used for molecular weight determinations in this investigation are simply those outlined in the instrument manual. The only major deviation was changing the recommended waiting between measurements from 2 to 5 min. The latter time was determined by an optimization technique described in the instrument manual that used a recorder to measure the voltage output as a function of time. Pyridine was chosen for the solvent vehicle, and the calibration constant was determined using reserpine (Aldrich 99% purity, molecular weight = 608.69). The sample chamber of the instrument was thermostatically controlled at 50°C. Only the room temperature soluble species of a sample could be analyzed. For this reason, the previously dried sample was first dissolved in pyridine using mild (80 watt) sonication. The solution was then filtered, and the pyridine was driven from the sample by drying for 24 hr in a vacuum oven evacuated

to 250 mm Hg and swept by nitrogen. The sample was then ready for preparation of the required solutions.

The use of vapor pressure osmometry to determine average molecular weights is a relatively simple technique. The inherent limitation is that the number average molecular weight determined by this method is biased toward species of low molecular weight. For this reason, the average molecular weights reported in this investigation may seem low compared to those which are averaged on a different basis.

5. Nuclear Magnetic Resonance

Many investigations have used nuclear magnetic resonance as an analytical tool to study coal derived compounds.[43-47] In the case of ^{1}H-NMR spectroscopy, these compounds are characterized by the chemical environment of their protons, as shown by the resonance peaks in given regions of the spectrum. For example, hydrogen connected to an aromatic ring generally produces a peak anywhere from 5.8 to 8.8 ppm* downfield from a reference tetramethylsilane resonance.[44]

Such considerations have led to the division of an NMR spectrum into general regions characterized by the type of proton environment. Investigators do not always agree on the location or range of these regions, but a general consensus exists that aromatic protons produce peaks from roughly 6 to 9 ppm and that aliphatic protons are found from 0 to 5 ppm.

It was decided to use the method of Anderson for analysis of the ^{1}H-NMR spectra obtained in this investigation.[47] His work suggests the following four regions of proton resonances: aromatic and phenolic

*A down field shift of 180 Hz from tetramethylsilane equals 1.0 ppm.

protons from 6.00 to 8.67 ppm (Harom), hydrogen on saturated carbon adjacent to an aromatic ring from 2.00 to 3.33 ppm (Halpha), methylene or methine protons of saturated compounds or methylene, methine, or methyl protons beta or further from an aromatic ring from 1.00 to 2.00 ppm (Hbeta), and hydrogen on methyl groups of saturated compounds or those gamma or further from an aromatic ring from 0.50 to 1.00 ppm (Hgamma).

Sample preparation for NMR analyses was similar to the procedure outlined for vapor pressure osmometry. The extract material was dried for 24 hours at 130°C in a vacuum oven evacuated to 250 mm Hg and swept by nitrogen. The sample was then dissolved (at room temperature) in pyridine using mild (80 watt) sonication, filtered, and redried under the same conditions. Approximately a 50 mg portion of this material was then dissolved in 0.75 ml of d_5-pyridine (Aldrich 100% Gold Label) in a dry bag to insure the absence of moisture. This solution was again filtered through a 2 ml fritted glass filter (ASTM 10-15 M) and transferred to the NMR tube where one microliter of tetramethylsilane was added.

The ^{1}H-NMR spectra were obtained on the pulsed (Fourier transform) 180 MHz "Universal NMR Spectrometer" developed at the Department of Chemistry, University of California, Berkeley.[48]

III. RESULTS AND DISCUSSION

The interactions of a number of specific solvents with subbituminous coal were studied in the temperature range from 100 to 350°C. The nature of both the extracted material and the residual coal were characterized by various analytical techniques. The product gases were also analyzed for their quantity and composition.

A. Experiments Performed

The contacting solvents studied in this investigation (except tetrahydrofuran) are classified as organic, amine bases. They were pyridine, quinoline, piperidine, ethylenediamine, ethanolamine, and tetrahydrofuran. The yield of dissolved material was studied as a function of contacting time at 250°C with piperidine and pyridine. All other coal/solvent contacting experiments were conducted for 4 hr, giving extraction to between 60 and 70% of completion.

B. Principal Results

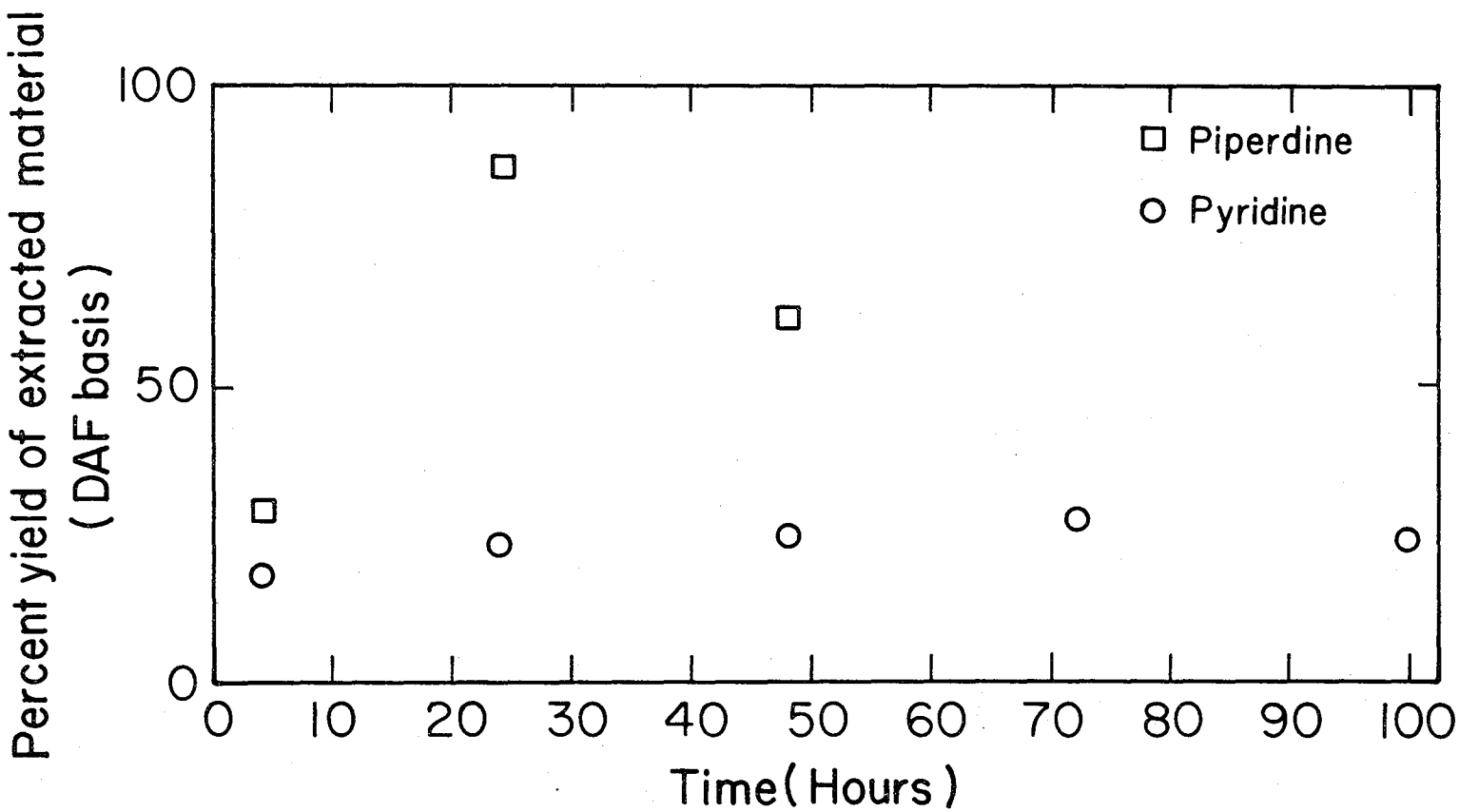
The immediate results obtained from coal/solvent contacting are the yields of extracted material, elemental analysis of the dissolved material and residual coal, and product gas analysis. With these data elemental material balances can be made, and the extent of incorporation of solvent in extraction products can be calculated.

Retention (or incorporation) of solvent in extraction products has been observed in many investigations of the action of various solvents on coal.[1,8,14,28,35] The occurrence of this phenomenon is even more prevalent with specific solvents, where chemical interaction between the free electron pair on the oxygen or nitrogen atom of the solvent and the reactive sites in the coal structure is

suspected. Incorporation of contacting solvent in either the residual coal or extracted material has a significant effect on the calculated value of extraction yield. Corresponding elemental analyses of carbon and hydrogen may also be in error because of the presence of solvent. An effort has been made in this study to correct the yields of extracted material, along with the elemental analysis of hydrogen and carbon, for the incorporation of solvent. In this discussion the extraction yield will always refer to (unless otherwise noted) the weight fraction of the extracted material, corrected for retained solvent, to the parent coal on a dry, ash-free basis. This is called the dry, ash and solvent-free yield, or simply daf yield. Likewise all reported hydrogen and carbon compositions are (unless otherwise noted) on a solvent-free basis. The correction for the amount of retained solvent in the dissolved material or the residual coal is based on the fact that the parent coal contains only a relatively small amount of nitrogen (0.97 wt%). Since all of the contacting solvents (except tetrahydrofuran) contain nitrogen, incorporation of these solvents in the extraction products is easily detected by elemental nitrogen analysis. The necessary assumptions, details of the correction calculations, and the original, uncorrected data are available in Appendix A.

1. Yield as a Function of Contacting Time

The effect of contacting time on the yield of extracted material was studied by sampling from the bulk solvent during exhaustive extraction. Such experiments were conducted with pyridine and piperidine at 250°C for 100 and 48 hr respectively. The results are represented by a plot of the yield of extracted material vs contacting time in Fig. 4.



XBL 779-1856

Fig. 4. Percent yield of extracted material as a function of contacting time using piperidine or pyridine at 250°C.

Some of the values for the yield of extracted material, as determined by sampling through the bulk sampling line, are apparently too high for both pyridine and piperidine extractions. This is due to the fact that, at the moment of sampling, the contacting cup (150 ml) and condenser may both contain an amount of pure solvent. This would make the observed concentration of the dissolved material in bulk solvent solution (500 to 700 ml) artificially high. An attempt was made to compensate for this effect, when performing the calculations, by assuming the contacting cup was half full and by estimating the amount of vaporized solvent at 250°C. In cases where only a small fraction of the original coal is dissolved, as with pyridine extraction, the discrepancy is not large. A considerable problem arises, as with piperidine, when a large fraction of the original coal is dissolved. For example, the yield of piperidine-extracted material calculated after 24 hr of contacting was 86.6%. This would become 69.3%, if the contacting cup were assumed full, and 104% if it were assumed empty. The final value of the yield of extracted material is unbiased since the apparatus is disassembled, and the total volume is completely mixed.

The purpose of conducting these exhaustive contacting experiments was to determine an ultimate yield of extracted material that could be compared to the results for shorter, more convenient contacting times. The ratio of the 4-hour to the ultimate yield gives a measure of the percent completion of the extraction process. For pyridine and piperidine, these values ranged roughly from 60 to 70%.

Table III. Summary of the Data Resulting from the Extraction of Roland Seam Coal with Pyridine, Quinoline, Piperidine, Ethylenediamine, or Tetrahydrofuran for 4 hours.

Solvent	Temp. (°C)	Residue				Extract				Extract Yield (% DAF Coal)	Balances				
		%H	%C	H/C	S[a]	%H	%C	H/C	S[a]		%H[b]	HMB[c]	%C[b]	CMB[c]	OMB[d]
Pyridine	100	4.45	50.87	1.05	0	8.50	75.98	1.34	0	9.4	4.51	90	49.88	84	94
Pyridine	150	4.60	55.16	1.00	0.002	8.54	76.36	1.34	0	10.4	4.87	97	56.09	95	98
Pyridine	200	4.27	52.58	0.970	0.014	8.00	76.04	1.26	0	13.1	4.58	91	53.87	91	97
Pyridine	200	4.25	57.53	0.886	0.027	8.49	76.66	1.33	0.006	13.7	4.62	92	58.17	98	97
Pyridine	250	4.01	52.52	0.916	0.040	7.32	73.93	1.19	0.031	16.6	4.32	86	53.49	90	96
Pyridine	250	3.84	51.17	0.900	0.027	8.17	75.95	1.29	0.010	15.9	4.23	84	51.93	88	95
Pyridine	300	3.77	60.69	0.745	0.041	8.08	77.66	1.25	0.016	19.9	4.20	84	58.76	99	92
Pyridine[e]	300	3.60	58.76	0.735	0.040	7.27	76.21	1.14	0.033	21.0	3.89	78	57.22	96	95
Pyridine[f]	250					7.77	73.32	1.27	0.044	17.6					
do. (24 hr)						7.14	72.02	1.19	0.068	23.3					
do. (48 hr)						7.28	73.94	1.18	0.054	24.5					
do. (72 hr)						6.86	72.24	1.14	0.068	27.6					
do. (100 hr)		3.48	55.83	0.748	0.046	7.37	76.34	1.16	0.028	24.5	4.01	80	55.66	94	92
Quinoline	200	3.43	56.20	0.732	0.092	6.25	69.17	1.08	0.25	15.0	3.51	70	53.35	90	92
Quinoline	250	3.11	55.76	0.669	0.092	5.34	64.72	0.990	0.29	25.0	3.40	68	54.34	92	94
Quinoline	250	2.98	51.76	0.691	0.098	4.46	61.05	0.877	0.48	30.4	3.40	68	54.78	92	101
Quinoline	300	2.71	55.84	0.582	0.14	4.79	67.20	0.855	0.37	30.3	2.90	58	51.72	87	87
Quinoline	350	2.21	54.27	0.489	0.28	4.57	75.74	0.724	0.80	29.4	2.30	46	47.30	80	77
Quinoline[e]	350	2.52	54.78	0.552	0.32	4.92	79.04	0.747	0.99	32.4	3.16	63	57.42	97	105
Piperidine	105	4.00	59.36	0.809	0.19	7.88	75.65	1.25	0.24	7.5	3.87	77	54.76	92	90
Piperidine	150	3.01	60.29	0.599	0.23	7.40	78.31	1.13	0.47	8.6	2.70	54	49.06	83	79
Piperidine	200	3.49	57.96	0.723	0.19	6.27	75.42	0.998	0.38	18.9	3.70	74	56.93	96	93
Piperidine	250	3.27	57.43	0.683	0.23	5.92	78.37	0.906	0.60	35.4	3.93	78	61.41	104	96
Piperidine[e,f]	250					5.79	77.62	0.895	0.59	28.4					
do. (24 hr)						5.56	79.87	0.835	0.75	86.6					
do. (48 hr)		3.21	50.39	0.764	0.26	5.31	79.23	0.804	0.79	62.3	4.54	91	69.04	116	100
Ethylenediamine	150	3.36	59.65	0.676	0.16	2.66	74.22	0.430	0.62	42.4	3.00	60	62.97	106	97
Ethylenediamine	200	2.68	52.85	0.608	0.17	3.43	74.70	0.551	0.58	48.0	2.87	57	59.42	100	95
Ethylenediamine	250	1.83	51.84	0.424	0.18	3.26	85.37	0.458	0.56	64.3	2.51	50	67.37	114	95
Tetrahydrofuran	150	4.90	61.80	0.952	—	9.90	78.54	1.51	—	7.4	5.18	103	62.36	105	100
Tetrahydrofuran	200	4.50	53.40	1.01	—	9.28	77.61	1.44	—	8.7	4.78	95	54.28	92	98
Tetrahydrofuran	200	4.53	55.91	0.972	—	9.67	78.20	1.48	—	9.3	4.94	99	58.00	98	101

a) Weight ratio of retained solvent to solvent-free extract.

b) Wt% of combined hydrogen or carbon from elemental mass balance.

c) Wt% recovery of the original amount of hydrogen (5.01%) or carbon (59.28%) from the coal in the extract, residue, and gas (when analyzed).

d) Wt% recovery of the original amount of coal in the extract, residue, and gas (when analyzed).

e) Runs in which product gases were analyzed.

f) Extended extraction; first sample obtained after 4 hours.

In a similar study, Draemel reported a 70% attainment of the ultimate yield of material extracted by tetralin at 200°C for 4 hr.[8]

These results indicate that exhaustive extraction of subbituminous coal is not necessary to compare the ability of different contacting solvents to dissolve coal. Comparisons may be made using 4-hr extraction times and be expected to give representative results. Additionally, the amount of coal dissolved after 4 hr of contacting is roughly proportional to the total amount attainable after exhaustive extraction.

2. Results of Specific Solvent Contacting

The principal data resulting from the interaction of specific solvents with a subbituminous coal are summarized in Table III. The dependence of the yield of extracted material on the temperature of coal/solvent contacting is represented in Figs. 5a and 5b. Table III presents the elemental hydrogen and carbon composition, the molecular H/C ratio, and the fraction of retained solvent of both the extract and residue. An elemental hydrogen and carbon mass balance is calculated from the corrected compositions of the extracted material and residual coal using the equation:

$$\left[\text{Extract Yield}\right]\left[(\text{C,H})\ \text{wt\%}\right]_{\text{Extract}} + \left[\text{Residue Yield}\right]\left[(\text{C,H})\ \text{wt\%}\right]_{\text{Residue}} + \left[\text{Gas Yield}\right]\left[(\text{C,H})\ \text{wt\%}\right]_{\text{Gas}}{}^{*} = \left[(\text{C,H})\ \text{wt\%}\right]_{\text{Combined}} \qquad (1)$$

In Eq. (1) the yield (weight fraction of original coal as extract, residue, or gas) are on a dry only basis, or, corrected for solvent retention but not for ash. The wt% recovery of the original hydrogen

* This term is included in Eq. (1) only in cases where the product gas was analyzed.

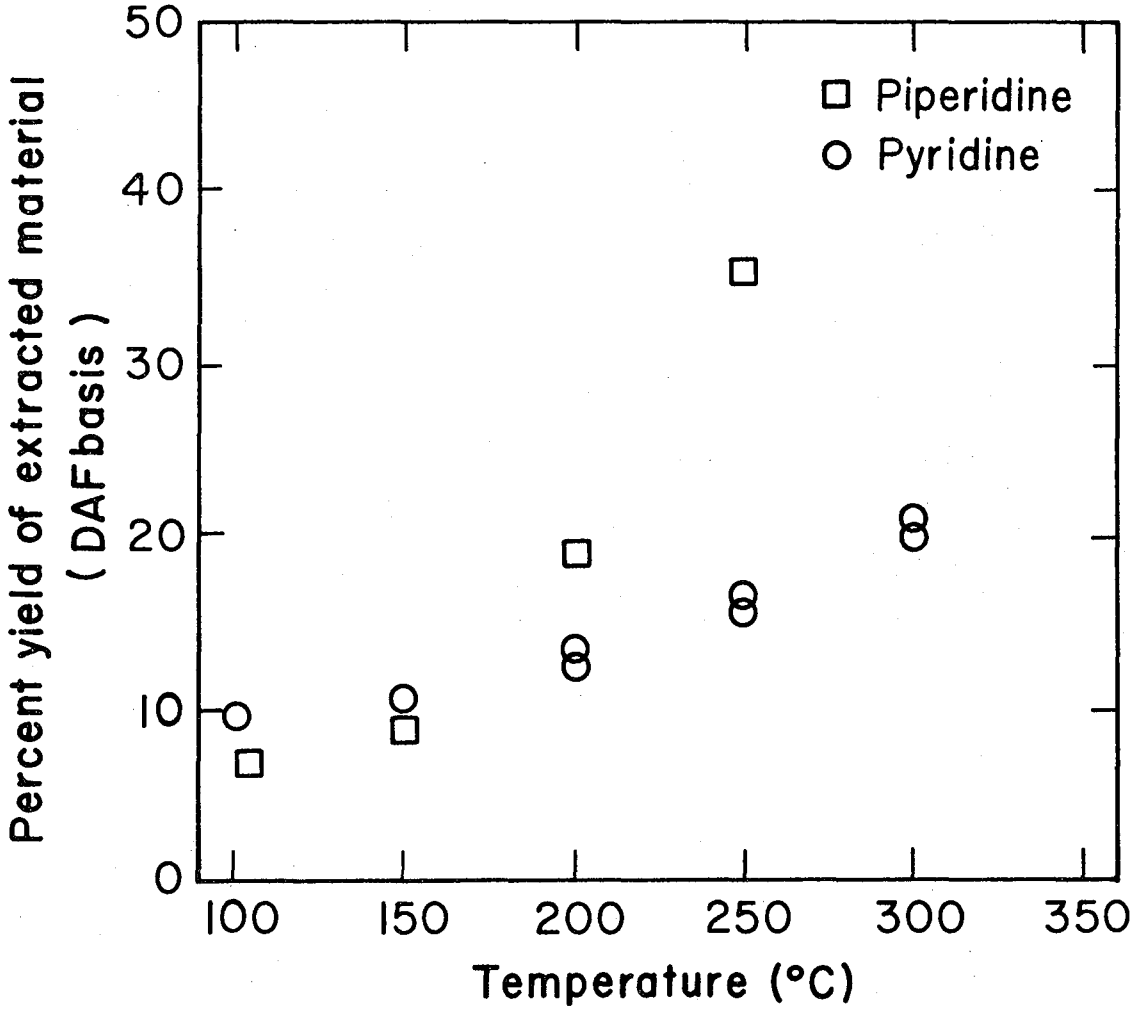


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Fig. 5a. Percent yield of extracted material as a function of contacting temperature using piperidine or pyridine.

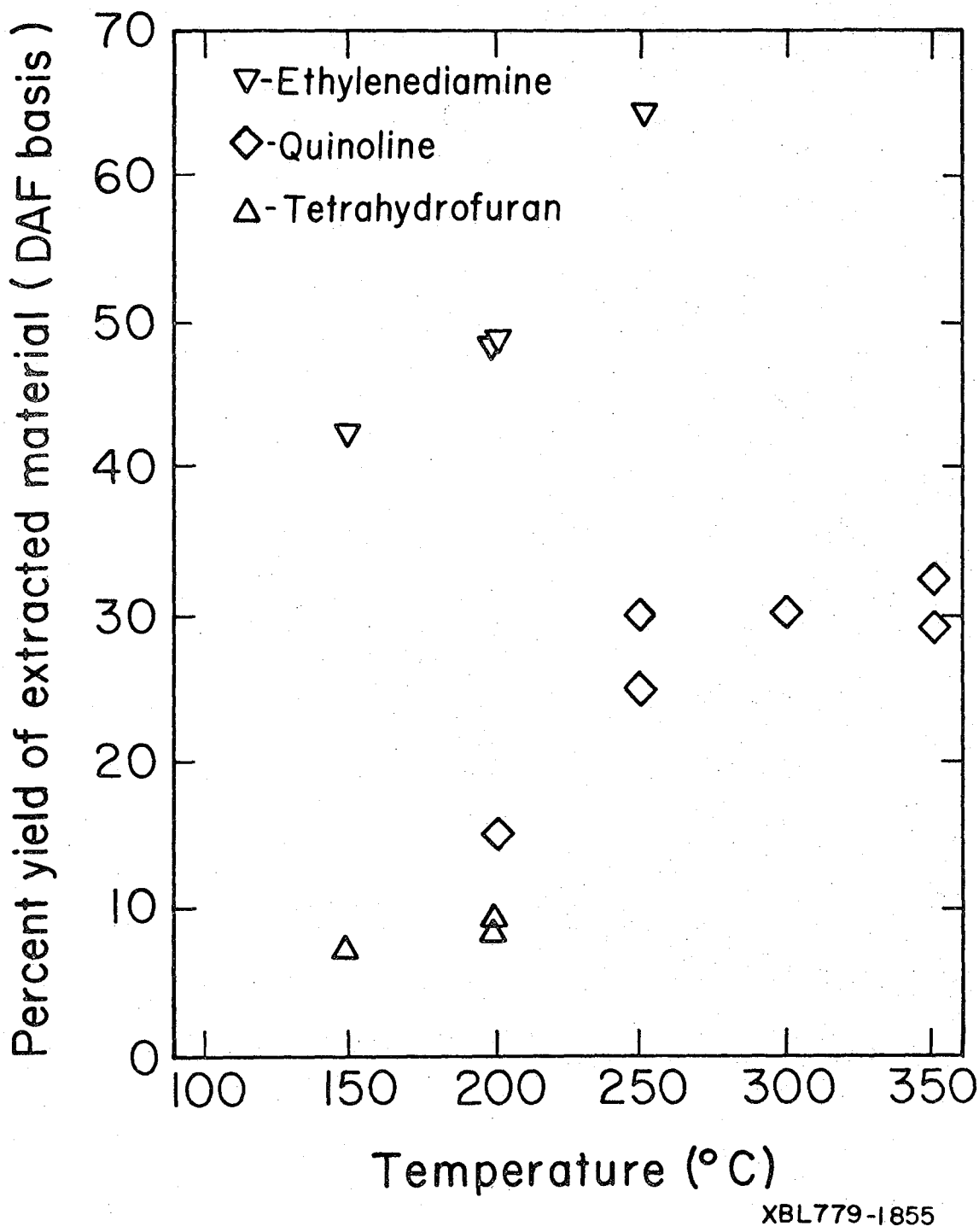

Fig. 5b. Percent yield of extracted material as a function of contacting temperature using ethylenediamine, quinoline or tetraphydrofuran.

(5.01%) or carbon (59.28%) from the coal in the extract, residue, and gas (when analyzed) is labelled "HMB" or "CMB" respectively in Table III. The overall material balance, labelled "OMB" in Table III, is the wt% of original coal recovered in the extract, residue, and gas (when analyzed). Any overall material balances far below 100% are probably the result of product gas evolution or a loss of material in handling.

Pyridine is probably the most extensively studied of all specific solvents.[31,36,30,28] Its solvent power has been observed to generally decrease with decreasing rank of coals.[30,31] As an organic base of intermediate strength (pKb = 8.75), powerful interactions of the acid-base type are not expected to occur with subbituminous coal.[49]

The results shown in Fig. 5a verify that pyridine is only moderately effective in dissolving subbituminous coal. It also appears that changing the temperature of coal/solvent contacting has only a slight effect on the yield of extracted material. Over a temperature range of 200°C the fraction of dissolved coal roughly doubles from 9.4% at 100°C to 21% at 300°C. Dormans and van Krevelen have also observed a weak influence of temperature on the extraction of a higher rank coal (84% carbon) with pyridine.[31] Increasing the contacting temperature by 160°C increased the yield of extracted material from 23% at 20°C to 34% at 180°C.

The data in Table III indicate that the hydrogen and carbon mass balances for pyridine extractions are quite good. Duplicate experiments were performed at contacting temperatures of 200, 250, and 300°C to

check the precision of the data. These checks show that the procedure of coal/solvent contacting, used in this investigation, is quite reproducible.

The nature and quantity of the product gases resulting from pyridine extractions at 300°C were analyzed by the previously described method. The gas composition was 87.2 wt% CO_2, 8.2% CO, 3.61% air,* 0.942% CH_4, with trace amounts of hydrogen. It represented a total product gas yield of 6.3% of the original dry, ash-free coal. The method for calculation of the amount of gas produced is presented in Appendix B.

The material extracted by pyridine retained little or no solvent. The weight ratio of solvent to solvent-free extract varied from 0 at 100°C to 0.033 at 300°C. Consequently, the solvent-free values presented in Table III and Fig. 5a differ only slightly from the original data.

Multi-ring aromatic solvents have been observed to have advantageous behavior for many coals. Quinoline both has this character and, with its free electron pair on the nitrogen heteroatom, satisfies the definition of a specific solvent. Its strength as an organic base (pKb = 9.06) is comparable to pyridine.[49] Hariri and Hill cite evidence that quinoline is a better solvent for a Utah bituminous coal than pyridine.[50] Much earlier, in 1940, Belcher had determined that quinoline was a slightly more effective solvent than pyridine; but he warned that exposure of technical grade quinoline to light resulted in the "synthesis of soluble material".[51] At its boiling point (238°C), the amount of degradation of technical quinoline was noticeably worse. However, a negligible amount of decomposition was observed when a "pure"

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* Assuming air consists of 78.08 mole% N_2, 20.95% O_2, 0.93% Ar, and 0.03% CO_2.

quinoline was subjected to the same tests. Johns, McElhill, and Smith observed the decomposition of quinoline to occur between 510 and 535°C at a rate of 1 mole% per hour.[52] The quinoline used in this investigation was 99.5% analytical reagent grade, and the maximum contacting temperature was 350°C. Decomposition of the quinoline was, therefore, not expected to be a problem.

Figure 5b seems to indicate quinoline is a more effective solvent for subbituminous coal than pyridine. The yield of material extracted by quinoline ranged from 15.0% at 200°C to 32.4% at 350°C. It should be noted that the independence of the yield of dissolved coal exhibited from 250 to 350°C is probably not a true effect. Near and above the coal pyrolysis temperature (325°C), a significant evolution of product gases was expected. Analysis of the gases, resulting from contacting the coal at 350°C with quinoline, confirm this anticipated result. The gas composition was 69.2 wt% CO_2, 16.2% CO, 6.38% CH_4, 3.32% H_2O, 2.54% air, 2.30% N_2 and 0.05% H_2. The total product gas yield was 32.0% of the original dry, ash-free coal.

Kiebler contacted a Pittsburg seam coal (77.5% carbon) in a sealed bomb with quinoline for 120 hr at 200°C and recovered organic material amounting to 17.4% of the original dry, ash-free coal.[28] Soxhlet-type extraction of a Utah bituminous coal for 120 hr at 120°C with quinoline dissolved 15.74% of the parent coal.[50] These results indicate that quinoline is probably a good solvent for subbituminous coal, since extraction at 200°C for only 4 hr resulted in a 15.0% yield of extracted material.

0 0 0 0 4 9 0 0 5 6 2 5

Table III summarizes the data regarding mass balances on hydrogen and carbon as well as the extent of incorporation of quinoline in the extracted matter. Although this investigation confirms that quinoline is more effective than pyridine in dissolving subbituminous coal, it was also observed that quinoline was incorporated to a much higher extent in the extracted material. The ratios of the weight of solvent to solvent-free extract ranged from 0.25 at 200°C to 0.99 at 350°C. It is evident that some strong interaction is taking place between the coal and the solvent, although the relatively weak basic character of quinoline would suggest that this interaction is not of the acid-base type.

The mass balances in Table III on carbon, resulting from the extraction of coal with quinoline are quite good, but those on hydrogen generally display an increasing hydrogen deficiency at higher temperatures. Judging from the amount of methane and water produced at 350°C, part of this loss of hydrogen could be due to the evolution of hydrogen-bearing product gases.

Piperidine was chosen for a contacting solvent because of its strong basicity (pKb = 2.877) and its classification as a specific solvent in the work of Dryden.[49,6] Although piperidine is the hydroaromatic analogue of pyridine, it is not expected to act as a hydrogen donor at the relatively low contacting temperatures of this investigation. Rather, its solvent power was anticipated to lie in the availability of the free electron pair on the nitrogen heteroatom and its interaction in acid-base manner with structures in the subbituminous coal.

From Figure 5a, it seems that the extent of interaction of piperidine with coal is a strong function of contacting temperature. The yield of extracted material ranged from 7.5% at 105°C to 35.4% at 250°C. Although piperidine appears less active than pyridine below 150°C, it dissolves more than twice as much coal as pyridine at 250°C. Dryden dissolved 27.5% of an intermediate rank coal (72% carbon) with piperidine near its boiling point (106°C) after 48 hr of Soxhlet-type extraction.[30] An attempt was made to compare Dryden's results to the value obtained in this study by extrapolating 27.5% to a 4-hr result of 16.5% (assuming a 60% complete extraction for 4 hr). This extrapolated value is somewhat higher than the 7.5% yield of extracted material obtained in the present study. This may be due partly to the use of different coals. However, it is more likely the result of use of a correction factor by Dryden, determined for each solvent, to account for the amount of retained solvent in the dissolved material. This factor was averaged over a broad range of coals for ethylenediamine but was determined for a single, higher rank coal (80% carbon) for monoethanolamine, piperidine, and pyridine. These factors were then used to correct the yield of extracted material for the retention of contacting solvent regardless of coal or extraction conditions.

The elemental hydrogen and carbon mass balances for piperidine extractions in Table III are generally good. Some discrepancies may be accounted for by experimental errors in handling or elemental analysis of the extracted material and the residual coal. The evolution of hydrogen, water, or light hydrocarbon gases during coal/solvent contacting would result in the elemental hydrogen balance being less

than 100% complete. The product gases, resulting from contacting coal with piperidine at 150°C, were analyzed for content and quantity. The composition of these gases was 81.77 wt% air, 14.98% N_2, 3.20% NH_3, 0.08% CH_4, and 0.01% H_2. This amount of product gases would represent a 17.4% yield of the original dry, ash-free coal; but the large amount of air in the gas sample indicates an air leak in either the sampling or the analysis. However, the presence of ammonia and the absence of carbon dioxide, that was so abundant in the other gas analyses, may indicate that an interaction occurred with piperidine that did not with the other solvents.

The amount of solvent retention in the extracted material generally increased with increasing yield and temperature. These values ranged from 0.24 at 105°C to 0.60 at 250°C. At the longer contacting time of 48 hours (250°C), the ratio of solvent retained to the extract rose to 0.79. The strong dependence of the amount of solvent retention and the yield of extracted material on the severity of extraction conditions suggests that strong interactions are occurring between the solvent molecules and the coal structure.

Ethylenediamine is another strong (pKb = 3.04) organic amine base.[49] Its consideration for use as a contacting solvent comes primarily from its increasing activity toward coals of lower rank reported by Dryden and van Krevelen.[30,4] Its aliphatic character, together with its active amino groups at each end of the molecule, make it a likely solvent to interact strongly with the acid sites in the coal structure.

The results depicted in Fig. 5b verify that ethylenediamine is a powerful solvent for a subbituminous coal. Even at the mild extraction

temperature of 150°C, a yield of 42.4% of dissolved coal was realized. Extraction at the highest temperature of 250°C increased the yield to 64.3%. Dryden attained a 47% yield of extracted material, when contacting his coal (72% carbon) with ethylenediamine near its boiling point (117°C) for 48 hours.[30] Hariri and Hill report an 18% yield of dissolved material from Utah bituminous coal resulting from Soxhlet-type extraction with ethylenediamine near its boiling point for 44 hr.[50] The actual temperature of the coal in the extraction thimble was reported as 85°C because of cooling of the reflux by the condenser. These results indicate that ethylenediamine is a powerful solvent for the low rank subbituminous coal used in the present investigation.

The elemental hydrogen and carbon balances for ethylenediamine extractions in Table III show some interesting results. While the material balance on carbon is reasonably good, there is a large deficiency of hydrogen in the extracted material. Comparing the elemental analysis for hydrogen in the parent coal (5.01%) to that of the extracted material (2.66 to 3.43%), one observed a hydrogen deficiency on the order of 2% of the weight of the coal. Dryden described a 2% deficiency in hydrogen of the room temperature extraction product of a bituminous coal (80% carbon).[35] In that study elemental nitrogen analysis showed that extracted material was 16.3% higher in nitrogen than the parent coal. This corresponds to an incorporation of roughly 0.54 of the ethylenediamine to the solvent-free extract. The present study observed ethylenediamine retention in the extract ranging from 0.56 at 250°C to 0.62 at 150°C. It seems that the temperature of coal/solvent contacting does not have any influence on the amount of ethylenediamine

incorporation. The hydrogen deficiency and the large amount of solvent incorporation suggest some interaction, resulting in the loss of hydrogen, between the amine solvent molecule and the coal structure. Dryden attributes some of the hydrogen deficiency to incorrectly adjusting the hydrogen composition for adsorbed solvent, when the solvent is actually chemically combined.[35] More discussion of the apparent loss of hydrogen in ethylenediamine extractions is presented later.

Monoethanolamine possesses two functional groups that could interact with both the acidic and basic components of the coal structure. Its strength as an organic base (pKb = 4.502) is comparable to ethylenediamine, and the hydroxyl group is capable of reacting with active basic sites in coal.[49] As with ethylenediamine, the activity of monoethanolamine has been observed to increase toward coals of lower rank.[30,4] Thus it was investigated for its action on subbituminous coal.

The results of the two contacting experiments conducted at 150 and 250°C with monoethanolamine are not included in Figs. 5a and 5b or in Table III, because results for blank runs, in which only solvent (no coal) was charged to the system, indicate that decomposition of monoethanolamine occurred at both 150 and 250°C.* For this reason, the monoethanolamine results have not been discussed. In the interest of completeness, the data has been included in Appendix A.

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* Unacceptable discoloration of the solvent was observed in a previous blank run, but it was attributed to the use of a Viton O-ring that was subsequently replaced by a copper gasket.

Tetrahydrofuran does not fit into the category of an organic amine base. It is a cyclic ether generally recognized as an excellent multipurpose organic solvent. It has been observed in this study that organic material, already extracted from coal by another solvent, is often readily soluble in tetrahydrofuran. The ability of this solvent to interact with the original untreated coal was, therefore, examined.

As depicted in Fig. 5b, tetrahydrofuran was used over the rather limited temperature range of 150 to 200°C, because of its very low normal boiling point (67°C). The pressure limitations of the apparatus would be exceeded at temperatures above 200°C. The yield of material extracted by tetrahydrofuran ranged from 7.4% at 150°C to 9.3% at 200°C. Comparison of tetrahydrofuran to the other contacting solvents used in this temperature range demonstrates that it is the least effective in dissolving subbituminous coal. It is interesting, however, that tetrahydrofuran is a more effective solvent in the temperature range of 150 to 200°C than are some solvents that are particularly strong at higher temperatures. For example, tetralin extraction of the same subbituminous coal at 200°C for 200 hr (using the same apparatus) dissolved only 7.01% of the original dry, ash-free coal.[8]

The amount of tetrahydrofuran (if any) retained in either the residual coal or the extracted material could not be effectively measured. Unlike nitrogen, the elemental analysis for oxygen is obtained by difference only. Results obtained in this way lack the precision necessary to detect the presence of tetrahydrofuran in the extraction products. The elemental mass balances on hydrogen and

carbon in Table III for tetrahydrofuran extractions are extremely good. This fact, along with the observed small percentage of coal dissolved, indicate that probably no significant interactions occurred between subbituminous coal and tetrahydrofuran at these low temperatures. In addition, there was only a small amount of gas which resulted from contacting the coal with tetrahydrofuran. Extraction at 200°C produced gases (amounting to 1.4% of the original dry, ash-free coal) with a composition of 66.83 wt% CO_2, 24.18% air, 8.09% CO, 0.65% N_2, 0.24% CH_4, and 0.02% H_2.

In summary, the results of the various coal/solvent contacting experiments indicate that the effectiveness of a nitrogen base type solvent in dissolving subbituminous coal below the coal pyrolysis temperature is roughly a function of that solvent's basicity. Within this general trend, however, other factors (such as steric effects) must be taken into account. Comparing the activity of the solvents used in this investigation at 250°C shows that ethylenediamine is the most effective. Although piperidine is slightly more basic, the small, aliphatic structure of ethylenediamine may be more effective in penetrating to the acid sites within the coal structure than the larger, non-planar piperidine molecule. Pyridine and quinoline are far less basic than either piperidine or ethylenediamine and are also considerably less effective in dissolving subbituminous coal. Pyridine is slightly more basic than quinoline, but quinoline is a better solvent. The reason for the greater interaction of coal with quinoline than with pyridine is not clear from the present data. As a cyclic ether, tetrahydrofuran does not fit in the same class as the other solvents;

it was the least effective in dissolving subbituminous coal. A similar observation of the relationship between the ability of a particular solvent to dissolve a butiminous coal and that solvent's basicity has been outlined by Halleux and Tschamler for a number of pyridine bases.[26]

The extent of solvent retention in either the extract or residue was a function of extraction conditions for a given solvent. As the time or temperature of contacting increased, so did the amount of solvent retention. However, the strongest bases combined with the extracted material even at their lowest temperatures. The ratios of combined piperidine and ethylenediamine to their respective solvent-free extracts were 0.24 at 105°C and 0.62 at 150°C.

The mass balances on carbon were generally quite good for all of the contacting experiments. A deficiency in hydrogen that was more prevalent at high temperatures was generally observed. The apparent loss of hydrogen could be the result of significant acid-base interactions between the solvent molecules and the coal structure.

Hydrogen may also be lost in the formation of hydrogen-containing components that are volatile at coal extract drying conditions (130°C) such as water, ammonia, or light hydrocarbons. The nature of the interactions resulting in the loss of hydrogen may become more apparent in the discussion of the character of the extracted material. The effect of correcting the elemental analyses of hydrogen and carbon for retained solvent is discussed later.

The quantity of gas produced in coal/solvent interactions is a function of contacting temperature. A large amount of product gas

evolution was observed above the coal pyrolysis temperature. The main constituents were carbon dioxide and carbon monoxide with smaller amounts of air, methane, and trace amounts of hydrogen. Some of the air is probably due to air absorbed in the coal structure. A normal background of air exists from the inability to completely degas the apparatus before coal/solvent contacting experiments.

C. Characterization of Extraction Products

The interaction of subbituminous coal with organic solvents gives rise to extraction products in the forms of dissolved coal (extract), undissolved coal (residue), and gas. The extent of coal dissolution in these solvents and the nature of the gaseous products has already been discussed. The extract and the residue were subjected to more detailed examination.

The molecular H/C ratios of both the extract and residue from each contacting experiment were calculated from their respective solvent-free elemental compositions. More extensive analyses were conducted with extracted material selected from representative contacting experiments. This material was examined for its number average molecular weight; proton nuclear magnetic resonance was used to study the chemical environment of the hydrogen. The extracted material was also separated into fractions consisting of oils, asphaltenes, preasphaltenes, and pyridine insolubles; these fractions were analyzed for their number average molecular weights.

1. Molecular Hydrogen to Carbon Ratio

Figure 6 depicts the molecular H/C ratio of the extracted material as a function of temperature for each of the contacting solvents used

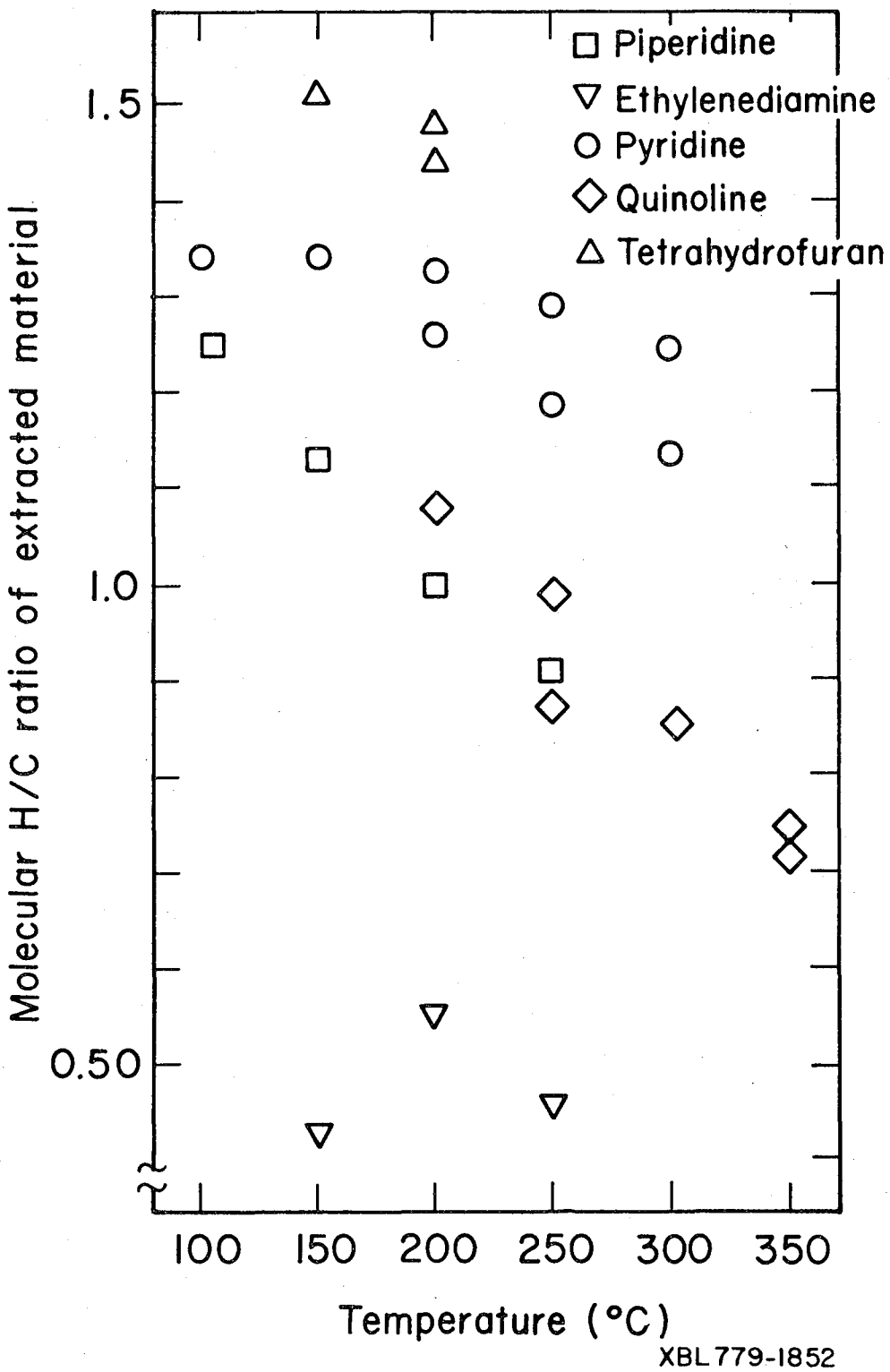

Fig. 6. Molecular H/C ratio of extracted material as a function of temperature with the various solvents.

in this investigation. The molecular H/C ratio of the original coal is 1.01. The general trend within each solvent is for the molecular H/C ratio of the extracts to decrease with increasing temperature. This behavior suggests that the lighter, hydrogen-bearing material is easily extracted at low temperatures. A more general relationship is plotted in Fig. 7. On this graph the molecular H/C ratio of the extract is presented as a function of the fraction of original coal dissolved by the different solvents at a number of temperatures. There is a clear general trend in which the molecular H/C ratio decreases with increasing yield of extracted material. This also indicates that the lighter, hydrogen-rich species are extracted under relatively mild conditions. As extraction is pushed to more severe conditions, components containing less hydrogen are extracted from the coal. Therefore, as the yield of extracted material increases, the H/C ratio of the total extract will decrease.

Figure 7 is also useful to compare how extensively each solvent interacts with the coal. Notice that the two weakest solvents (pyridine and tetrahydrofuran) always extract organic matter that is rich in hydrogen with respect to the parent coal. The yield of extracted material does not exceed roughly 20% using either of these two solvents. These results indicate that neither pyridine nor tetrahydrofuran is capable of significantly breaking apart the coal structure under these conditions. The solvents of intermediate strength (piperidine and quinoline) exhibit only a few cases in which the H/C ratio exceeds that of the parent coal. The rest are less than 1.01 with corresponding yields of extracted material exceeding 20%. These intermediate solvents

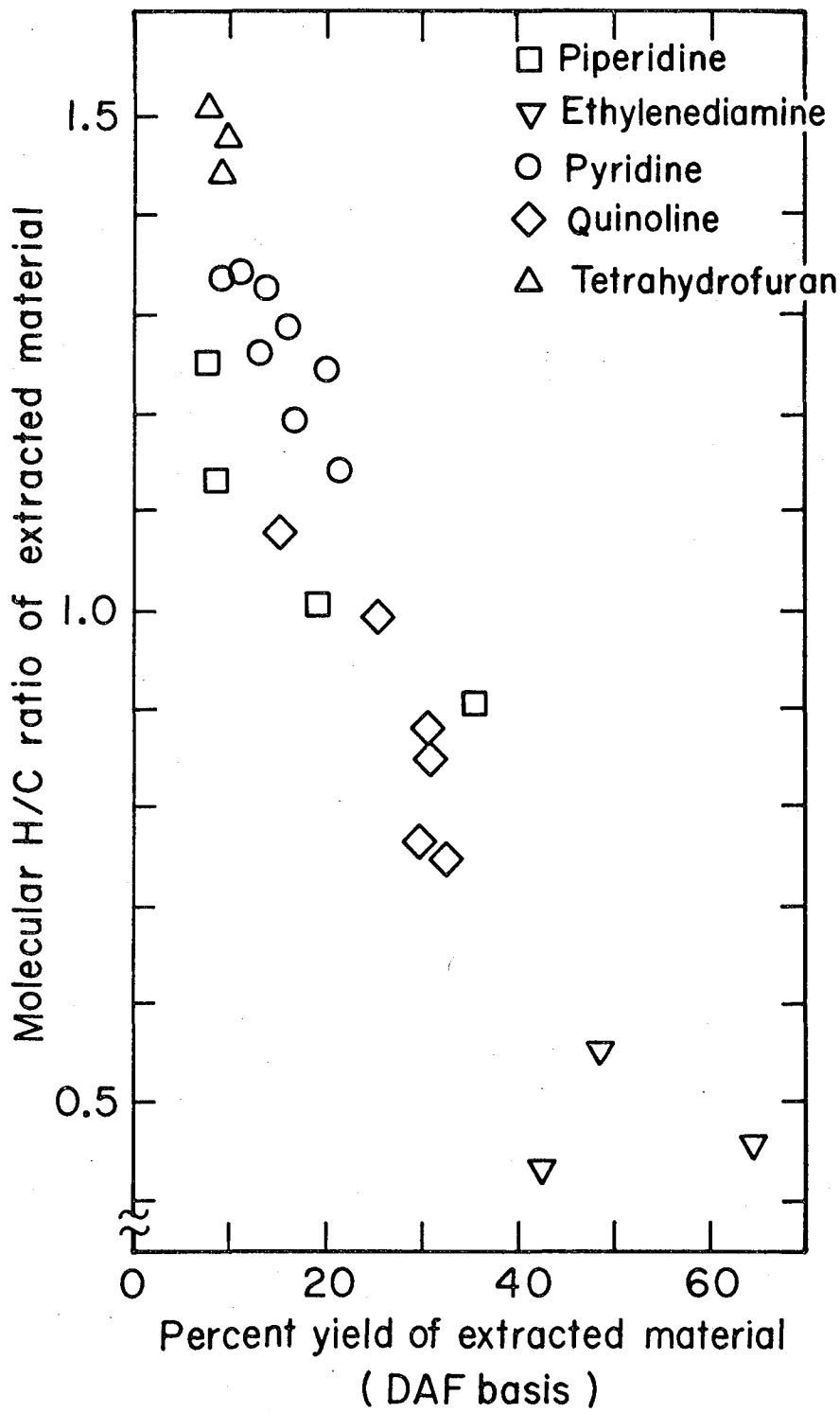

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Fig. 7. Molecular H/C ratio of extracted material as a function of the percent yield of extracted material.

are probably strongly interacting with the coal and breaking bonds in its structure. The strongest solvent (ethylenediamine) exhibits no particular relationship between the H/C ratio and yield of its extracted species. However, the extremely small H/C ratios of its extracts are accompanied by very high yields of extracted material. Extract H/C ratios in the area of 1.0 would suggest a breaking apart of the coal structure, which is consistent with the high yield of extracted material. Hydrogen to carbon ratios of roughly half that of the original coal may only be explained in terms of a coal/solvent interaction resulting in the loss of hydrogen.

2. Solubility of Extracted Material

The results of separating the coal extracts, obtained in this work, into oil (cyclohexane soluble), asphaltene (cyclohexane insoluble, benzene soluble), preasphaltene (cyclohexane and benzene insoluble, pyridine soluble), and pyridine insoluble fractions are summarized in Table IV. All yields reported represent fractions of the original dry, ash-free coal. All data have again been corrected to a solvent-free basis with the exception of the number average molecular weights. Many of the samples examined for molecular weight contained little or no retained solvent. Attempted corrections, applied to samples containing significant amounts of retained solvent, led to questionable results. All of the original, uncorrected data are presented in Appendix C.

An overall material balance has been presented in the final column of Table IV. This is simply the ratio of the sum of the weights of the oil, asphaltene, preasphaltene, and pyridine-insoluble fractions

Table IV. Summary of Data Concerning Fractions Obtained from Material Extracted by Pyridine, Piperidine, Ethylenediamine, and Quinoline from Coal.

Solvent (°C)	Extract				Oils				Asphaltenes			Preasphaltenes				Pyridine-insol.	
	% DAF	H/C	%S[a]	M_N[b]	% DAF	H/C	%S[a]	M_N[b]	% DAF	H/C	%S[a]	% DAF	H/C	%S[a]	M_N[b]	% DAF	O+A+P+P$_i$[c] / Extract
Pyr (150°C)	10.4	1.34	0	--	4.2	1.70	0	590	1.1	1.26	0	4.7	1.04	0.08	1440	0.0	96%
Pyr (200°C)	13.7	1.33	0.006	--	5.2	1.71	0	560	1.4	1.27	0	6.7	1.03	0.07	1530	0.0	97%
Pyr (250°C)	15.9	1.29	0.01	--	5.9	--	--	530	1.9	1.31	0.006	7.6	1.04	0.07	1740	0.0	97%
Pyr (250°C)	15.9	1.29	0.01	--	5.1	1.68	0	--	1.8	--	--	8.5	--	--	--	0.0	97%
Pyr (300°C)	21.0	1.14	0.03	--	5.0	1.66	0	440	3.1	1.16	0.02	12.8	0.967	0.06	400	0.0	100%
Pip (250°C)	35.4	0.906	0.60	1200	9.4	1.13	0.85	560	8.7	0.632	0.92	11.5	0.392	0.92	--	0.2	85%
Etdia (250°C)	64.3	0.458	0.56	770	0.0	--	--	--	0.0	--	--	25.4	0.084	0.79	--	35.5	95%
Quin (250°C)	25.0	0.990	0.29	580	4.2	1.51	0.39	400	2.5	1.33	0.47	15.4	1.06	0.45	--	0.3	90%

a) Weight ratio of solvent to solvent-free extract.

b) Number average molecular weight.

c) Wt% recovery of the original amount of coal extract in the oil, asphaltene, preasphaltene, and pyridine-insoluble fractions.

to the weight of the original coal extract. The amount of retained contacting solvent has been monitored across each of the three fractions by elemental analyses for carbon, hydrogen, and nitrogen. Likewise, the molecular H/C ratio has been calculated for each fraction. Number average molecular weights were determined for all of the oil fractions but for none of the asphaltenes. In most cases there was not a sufficient amount of asphaltene sample for molecular weight determination by vapor pressure osmometry. Only the preasphaltenes resulting from coal/pyridine contacting expriments were analyzed for their number average molecular weight since these wre the only preasphaltene fractions soluble in pyridine at room temperature. Not all of the material extracted from coal at 250°C by piperidine, ethylenediamine, quinoline, and tetralin was soluble in pyridine. For this reason, the number average molecular weight of the coal extract represents that of the room temperature pyridine-soluble portion. The material resulting from pyridine extraction at 250°C was consumed in other analyses and was not available for molecular weight determination.

The effect of the temperature of coal/pyridine contacting on the relative amounts of the resulting oil, asphaltene, and preasphaltene fractions is represented in Fig. 8. Notice that the preasphaltene fraction is the largest of the three at any temperature. Next largest are the oils, with the asphaltenes being the smallest fraction by far. The fraction of preasphaltenes increases with temperature from 4.7% at 150°C to 12.8% at 300°C as does the asphaltene fraction from 1.1% at 150°C to 3.1% a 300°C. The amount of oils, however, increases only slightly from 4.2% at 150°C to between 5.9 and 5.1% at 250°C

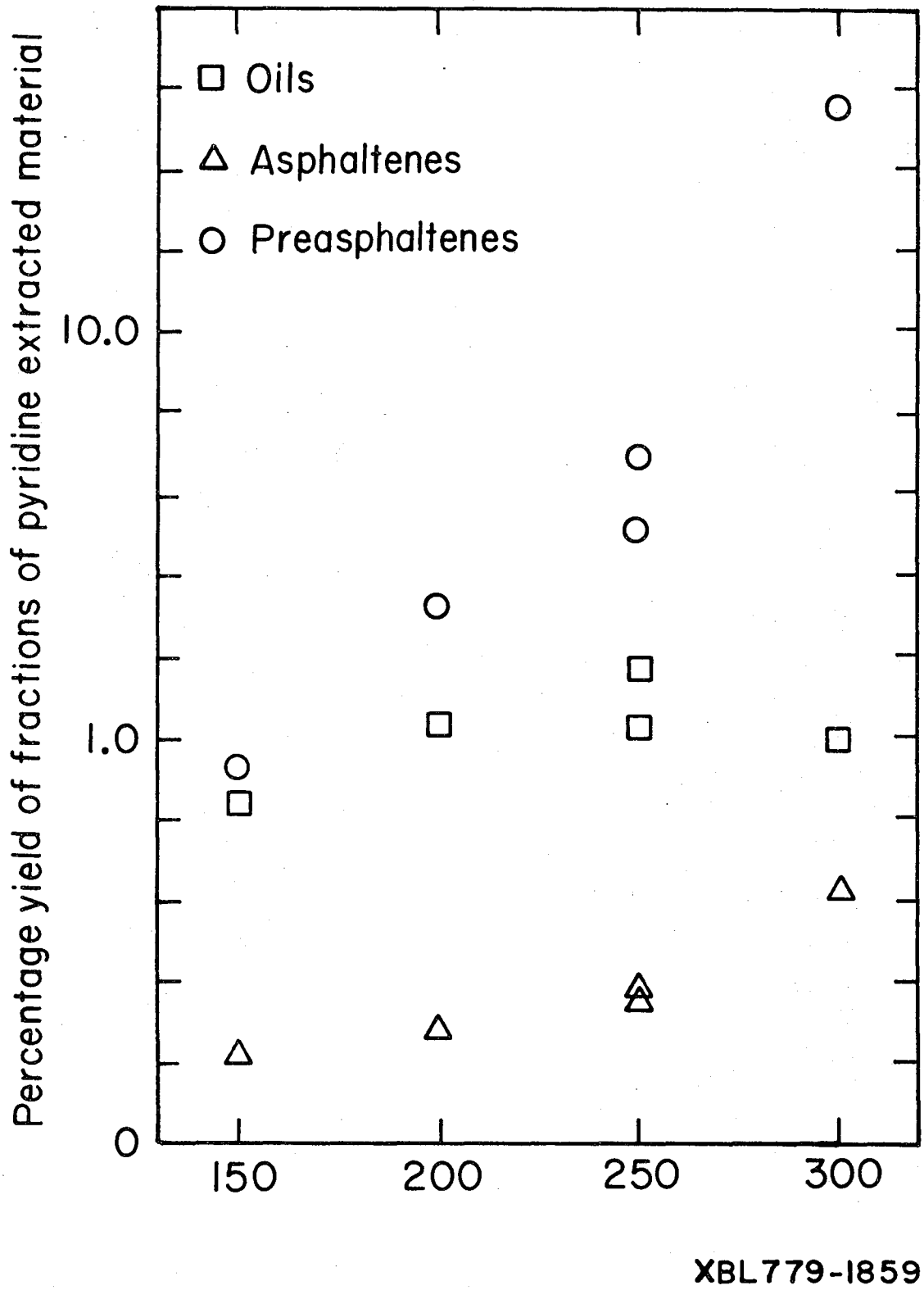

Fig. 8. Percent yield of fractions of pyridine-extracted material as a function of contacting temperature.

and remains essentially unchanged (5.0%) at 300°C. This behavior is consistent with the earlier obsrvation that the H/C ratio of the extracted material decreases with an increase in contacting temperature. The oils, having characteristically high H/C ratios from 1.66 to 1.70, are most easily extracted at low temperatures. Increasing the temperature only produces more of the material that is insoluble in cyclohexane and has a lower H/C ratio. This is reflected by the small, but steady, increase in the fraction of asphaltenes with temperature. Asphaltene molecular H/C ratios range from 1.16 at 300°C to 1.27 at 200°C. The sharp increase in the size of the preasphaltene fraction with temperature further demonstrates that at greater yields of extracted material progressively more components with low H/C ratios are extracted from the coal.

These observations are supported by the relation between the number average molecular weight of the extracted species and the contacting temperature, as shown in Fig. 9. As the temperature increases, the molecular weight of the preasphaltenes increases from 1440 at 150°C to a maximum of 1740 at 250°C. Along with a higher yield of extracted material, the increase in temperature results in the extraction of increasingly larger fragments. Finally, at 300°C the more severe conditions break apart these fragments into smaller species with a number average molecular weight of 1400.

The behavior of the molecular weights of the oil fraction with temperature may be explained similarly. The molecular weight remains essentially unchanged from 150°C to 250°C, since further extraction produces larger fragments that are not soluble in cyclohexane.

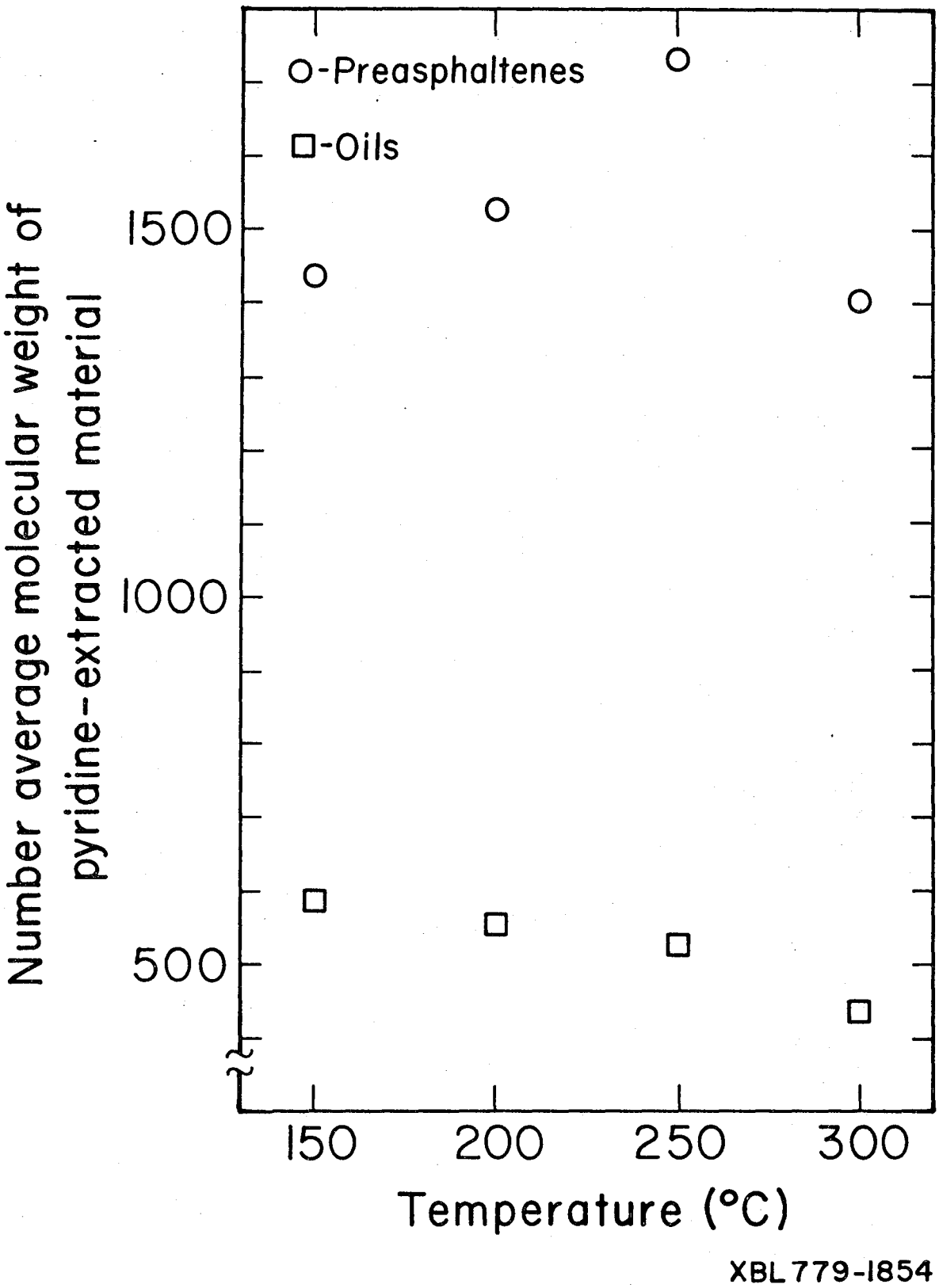

Fig. 9. Number average molecular weight of pyridine-extracted material as a function of contacting temperature.

However, at 300°C the molecular weight of the oils drops significantly to 440. This may be caused by the thermal degradation of the material into smaller species at this high temperature. It should be noted that the collective decrease in the size of the species produced at 300°C has probably been amplified due to the bias of a number average molecular weight toward low weight molecules.

The overall material balances presented in the final column of Table IV are quite good. The two 250°C pyridine extracts were sampled from the same contacting experiment. The results are close enough (within 3 to 7% of their averages) to justify reporting the average of these two values in any future discussions. Another sample has not been included since the originally extracted material was not properly filtered after the contacting experiment.

The amounts of the oil, asphaltene, preasphaltene, and pyridine-insoluble fractions resulting from contacting at 250°C with pyridine, quinoline, piperidine, and ethylenediamine are shown in Fig. 10. The height of each bar corresponds to the fraction of the original coal dissolved on a dry, ash and solvent-free basis.

The size of the oil fractions ranged from negligible with ethylenediamine to 9.4% with piperidine. Notice that piperidine produced almost twice as much oil as the next most effective solvent. The fact that ethylenediamine extract was insoluble in cyclohexane suggests it may consist of high molecular weight material.

Generally, only a small amount of asphaltenes were found on benzene extraction of the cyclohexane insolubles. The exception was

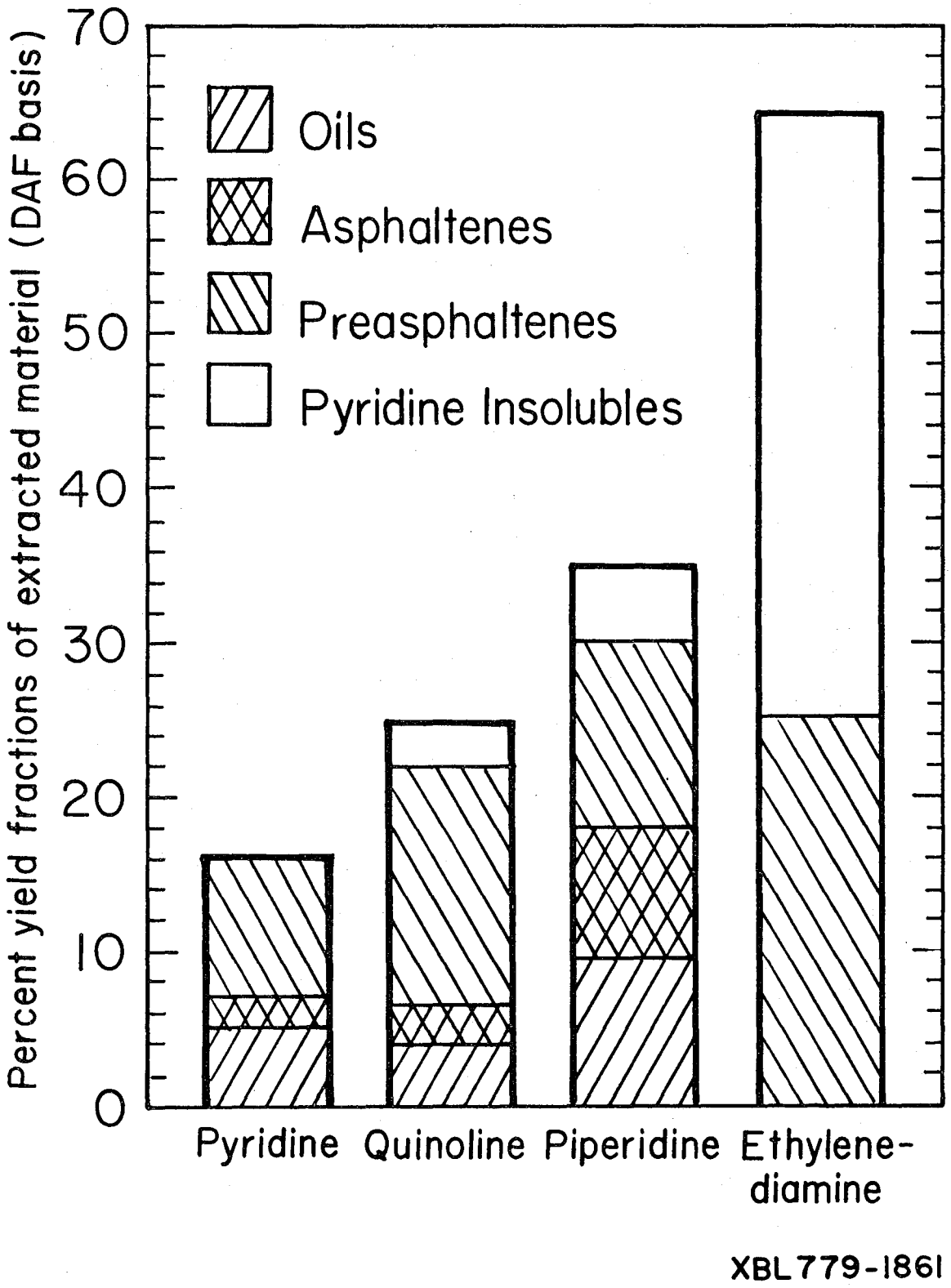

Fig. 10. Yield of fractions of coal extract.

the piperidine extract which contained an asphaltene fraction amounting to 8.7% in the ethylenediamine extract.

The largest of the three fractions of extracted material was that soluble in pyridine. The amount of these preasphaltenes ranged from 8.0% for pyridine extract to as high as 25.4% for ethylenediamine extract. Virtually all of the cyclohexane and benzene insoluble material was soluble in pyridine. The only contacting solvent that extracted a significant amount of pyridine-insoluble material was ethylenediamine. Any deficiency in the material balance (probably due to errors in the corrections for retained solvent) has been included with the pyridine insoluble fraction depicted in Fig. 10.

The data in Table IV summarize the character of the material extracted from coal by pyridine from 150 to 300°C and by piperidine, ethylenediamine, and quinoline at 250°C, as well as the oil, asphaltene, and preasphaltene fractions of these extracts. Of particular interest is the data concerning the extraction of coal with ethylenediamine. The extremely high yield (64.3%) of extracted material, containing so little hydrogen and of such limited solubility in pyridine, is unlike that for any other contacting solvent. In dissolving over half of the original coal, ethylenediamine is probably substantially breaking apart the coal structure. Under these conditions, large clusters of condensed hydroaromatic rings are expected in the extraction products. Highly substituted hydroaromatic clusters would probably not be soluble in cyclohexane or benzene and only slightly soluble in pyridine. The 0.56 ratio of retained ethylenediamine to the extracted material indicates some strong interaction between the coal structure

and solvent molecules. Blom and co-workers have indicated that as much as 30% of the total oxygen in a low rank coal may be attributed to carboxylic oxygen.[53] As a primary amine, ethylenediamine is capable of forming amides with these carboxylic acid groups. The water co-product would be lost under the drying conditions (130°C) of the residue and the extracted material. If it is assumed that each mole of retained ethylenediamine in the residue and the extract results in the formation of one mole of water, then 50% of the hydrogen from the coal not accounted for in extract and residue may be attributed to amide formation and subsequent loss of water. Similarly, if one-half of the ethylenediamine in the extract and residue were combined in amide formation, the required carboxylic oxygen woulld be about 50% of the total oxygen in the coal. This figure is probably too large, but these rough calculations indicate that a significant amount of the ethylenediamine retention and apparent loss of hydrogen may be attributed to the formation of amides.

If hydrogen is lost from the incorporated ethylenediamine, either in amide formation or through any other reaction, the correction for the hydrogen composition of the extract and residue will be in error. Continuing with the example of ethylenediamine extraction at 250°C, the H/C ratio of the extracted material would be increased from 0.458 to 0.583 by accounting for the loss of one hydrogen atom in the incorporated solvent. This corresponds to increasing the combined hydrogen content of the extract and residue (Table III) from 2.51 to 3.12 g per 100 g of dry coal, an increase of 24%.

Piperidine extraction of subbituminous coal also shows some interesting behavior as seen in Table IV. The material extracted by piperidine at 250°C has a higher degree of solvent retention than any other at that temperature. Coal contacting with piperidine has resulted in a much larger fraction of oils and asphaltenes than extraction with any other solvent. In addition, the molecular H/C ratio of the oil, asphaltene, and preasphaltene fractions seem unusually low. Since piperidine is a secondary amine, amide formation could partially explain the amount of piperidine incorporated into the extraction products and the deficiency of hydrogen in the extract and residue. Hydrogen lost in the form of water would account for 73% of the total hydrogen deficiency if one mole of water were produced for every mole of piperidine combined in both the extract and residue. If half of the total of incorporated piperidine combined in the form of amides, then 37% of the hydrogen deficiency can be attributed to the loss of water. This corresponds to the reaction of 37% of the total oxygen in the coal as carboxylic oxygen. The absence of CO_2 in the product gases also suggests amide formation since carboxylic acid groups are a potential source of CO_2. As in the case of ethylenediamine, any loss of hydrogen by the incorporated piperidine would yield an artificially low corrected hydrogen composition of both the extract and the residue. If the correction for solvent incorporated in the extract is adjusted for the loss of one hydrogen atom per molecule of piperidine retained, the H/C ratio of the extract is increased from 0.906 to 1.01. Extending this correction to the solvent incorporated in the residue increases

the combined hydrogen (Table III) from 3.93 to 4.34 g per 100 g of dry coal.

As a hydroaromatic, piperidine has the capability to provide hydrogen to the dissolved coal fragments. Although hydrogen-donor activity is not expected under such mild conditions (250°C), the high solubility of the extracted material in mild solvents such as cyclohexane and benzene is characteristic of the extracts of hydrogen transfer solvent. If, in donating its hydrogen, piperidine formed pyridine, the solution of dissolved coal could be checked for pyridine content. However, Nishiguchi and co-workers did not detect pyridine or any other low boiling dehydrogenation products after piperidine had successfully hydrogenated cyclopentene to cyclopentane at 180°C.[54] They suggest that the dehydrogenation intermediates from piperidine formed products of higher molecular weight.

These products would remain with the dissolved coal and probably be counted as retained solvent from the nitrogen analysis.

The number average molecular weight of piperidine extract (Mn = 1200) is probably valid since over 90% of it was soluble in pyridine at room temperature. The fact that it is much higher than 250°C tetralin extract* (Mn = 790) is probably because piperidine dissolved 35.4% (compared to tetralin's 8.02%) of the original coal; much of the piperidine extract consists of preasphaltenes that are probably of high molecular weight. The molecular weight of 778 obtained by Draemel for 250°C tetralin extract in benzene is comparable to the value of 790 obtained in pyridine for the same extract in this

*Sample obtained from Draemel.[8]

investigation.[8] Draemel reported the sample to be 82% soluble in room temperature benzene. A sample taken from the same stored concentrate of extracted material was found to be roughly 100% soluble in room temperature pyridine. Therefore, these two number average molecular weights are probably in agreement.

Some interesting comparisons can be made between the data resulting from pyridine and quinoline extractions of subbituminous coal at 250°C, presented in Table IV. The fact that quinoline is more effective in dissolving the coal is, in itself, surprising since pyridine is slightly more basic. The 1.29 molecular H/C ratio of pyridine extract is much greater than 0.99 value of quinoline extract. This may be due to the fact that the species of lower hydrogen content are contained in the preasphaltenes, and the size of the preasphaltene fraction of quinoline extract is about twice that for pyridine extract. The size and molecular H/C ratio of the oil and asphaltene fractions are really quite similar. The major differences between the two solvents are the much larger preasphaltene fraction etracted by quinoline and the higher degree of quinoline incorporation in the extracted material.

One considerable difference between quinoline and pyridine is the double ring structure of quinoline. This results in quinoline having a greatly extended pi-system of electrons above and below its planar structure. This feature, along with the electron pair on the nitrogen atom, allows quinoline to form very stable charge transfer sandwich complexes with phenol.[55] Low rank coals have been reported to contain phenolic hydroxyl groups that account for 15 to 22% of

the total oxygen content of the coal.[53] It is possible that complexes of this type are forming between quinoline and the phenolic groups available in subbituminous coal. This may explain the high degree of interaction between quinoline and subbituminous coal. If all of the retained quinoline in the extract and the residue were tied up in charge transfer complexes, the phenolic oxygen content of the coal would have to be at least 8.4% of the total oxygen in the coal. This is a reasonable number considering the reported values of 15 to 22% for phenolic oxygen in low rank coal.[53]

The number average molecular weight of 250°C quinoline extract of 580 is lower than that anticipated from its large preasphaltene fraction. As with ethylenediamine extract, this is probably because of the limited solubility of the extract in pyridine at room temperature. the reported molecular weight represents only roughly 60% of the sample of extracted material. The molecular weight of 400 for the oil derived from quinoline extract is comparable to that for piperidine extracts (Mn = 560) and those of pyridine extracts at various temperatures (Mn = 440 to 590).

3. Proton Nuclear Magnetic Resonance Studies

The ^{1}H-NMR spectra (180 MHz) of the material extracted from Roland seam subbituminous coal at 250°C with piperidine, ethylenediamine, quinoline, and tetralin are presented in Figs. 11 through 14. It should be remembered that these spectra represent the portion of the original extract soluble in d_5-pyridine at room temperature. This is roughly 90 to 100% for piperidine and tetralin extracts respectively. However, the ethylenediamine extract was only about 30% soluble, and

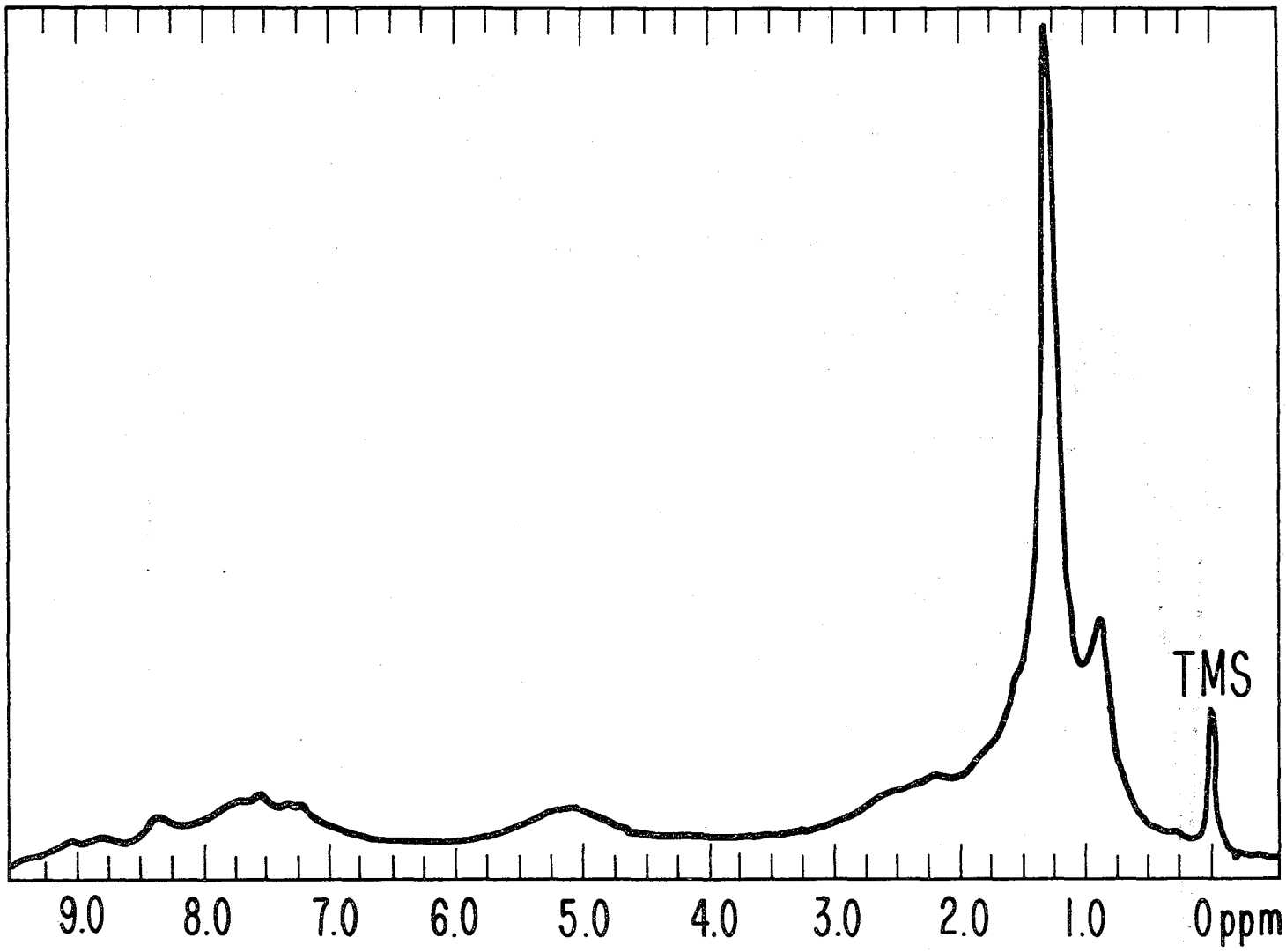

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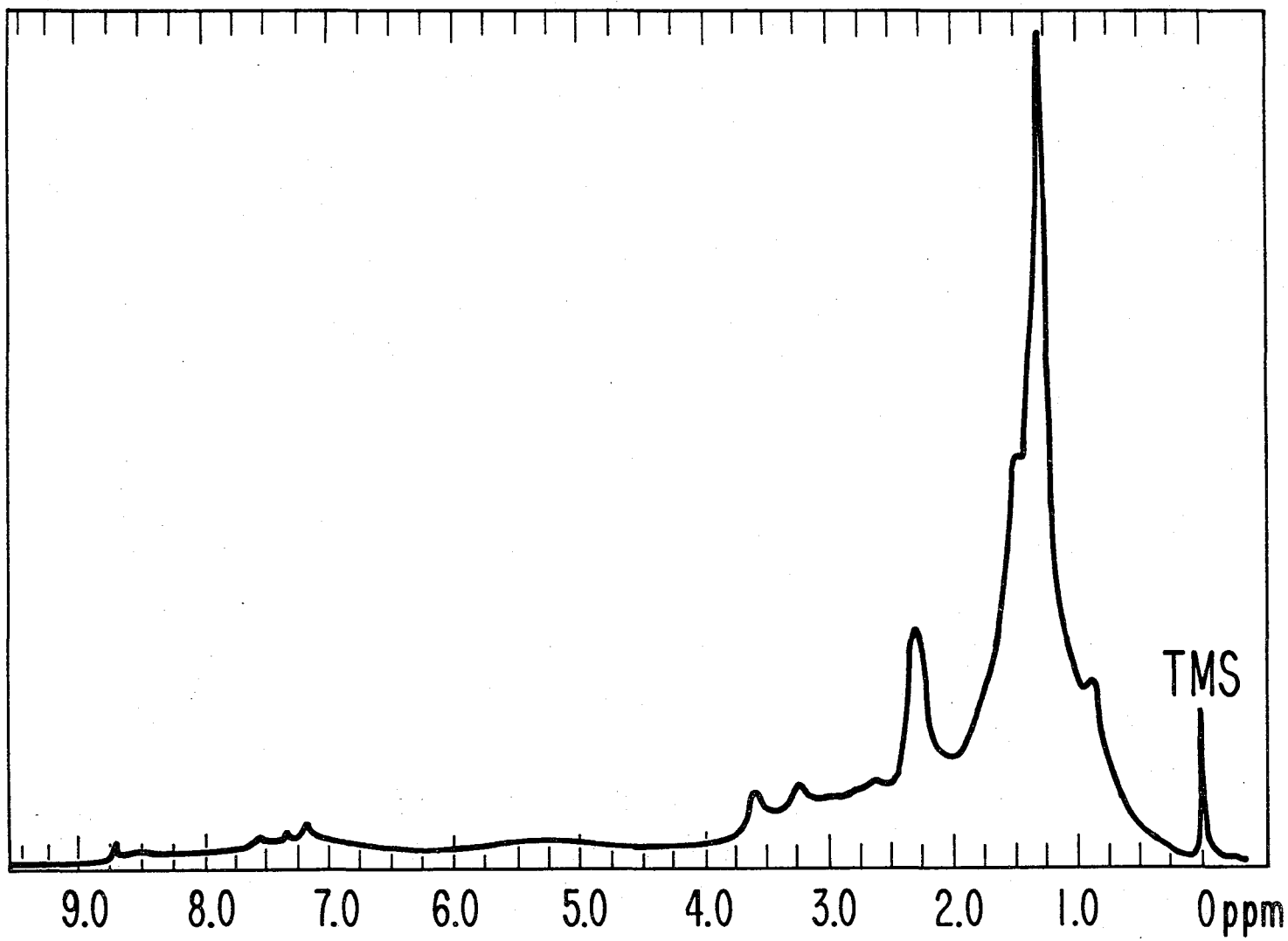
Fig. 11. ^{1}H-NMR spectrum (in d_5-pyridine) of the material extracted from Roland coal using quinoline at 250°C for 4 hr.

0 0 0 0 4 8 0 0 0 8 2



XBL779-1862

Fig. 12. ^{1}H-NMR spectrum (in d_5-pyridine) of the material extracted from Roland seam coal using piperidine at 150°C for 4 hr.

0 0 0 0 4 8 9 9 3 9 8

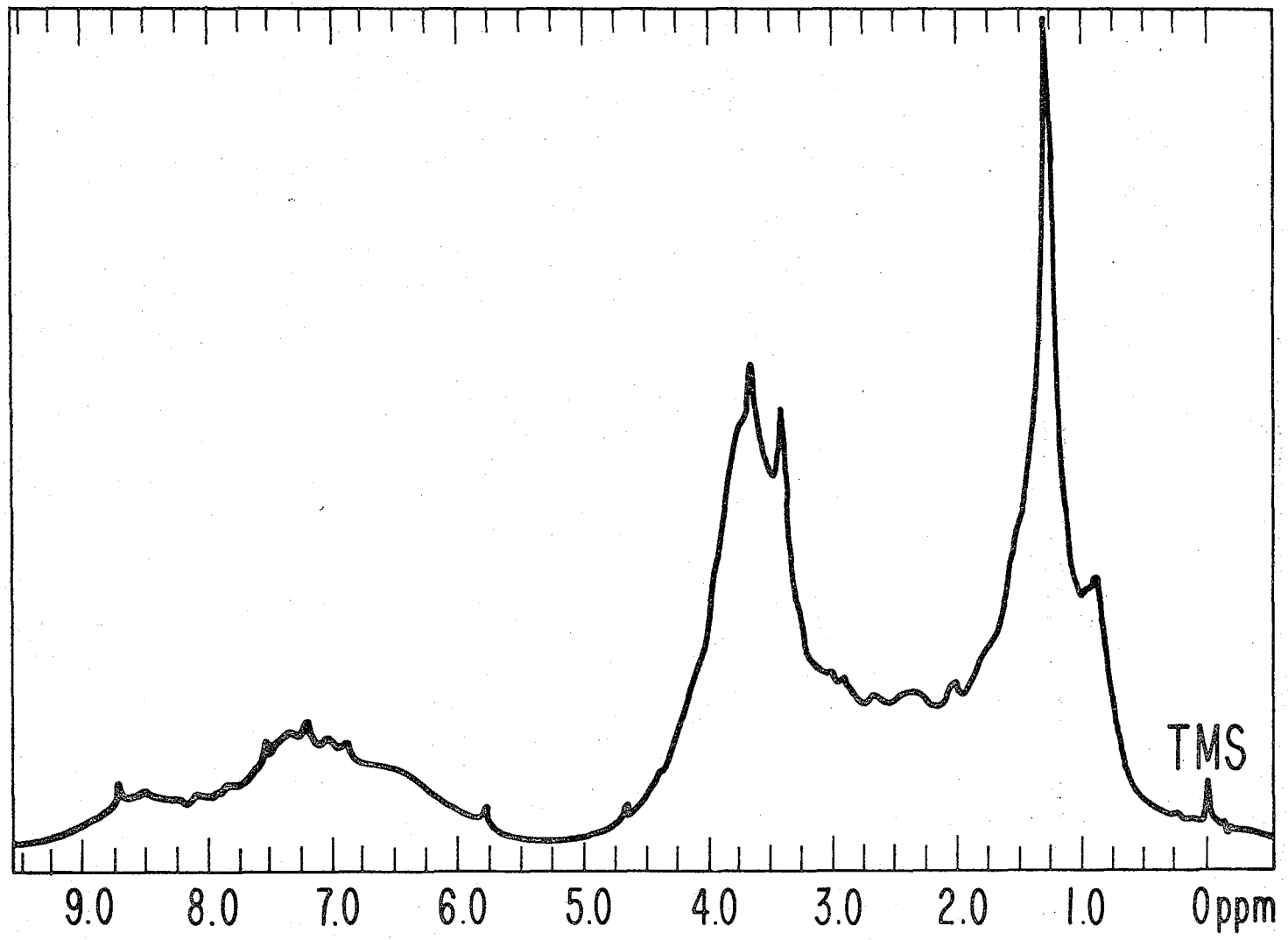


Fig. 13. ^{1}H-NMR spectrum (in d_5-pyridine) of the material extracted from Roland seam coal using ethylenediamine at 250°C for 4 hr. XBL779-1864

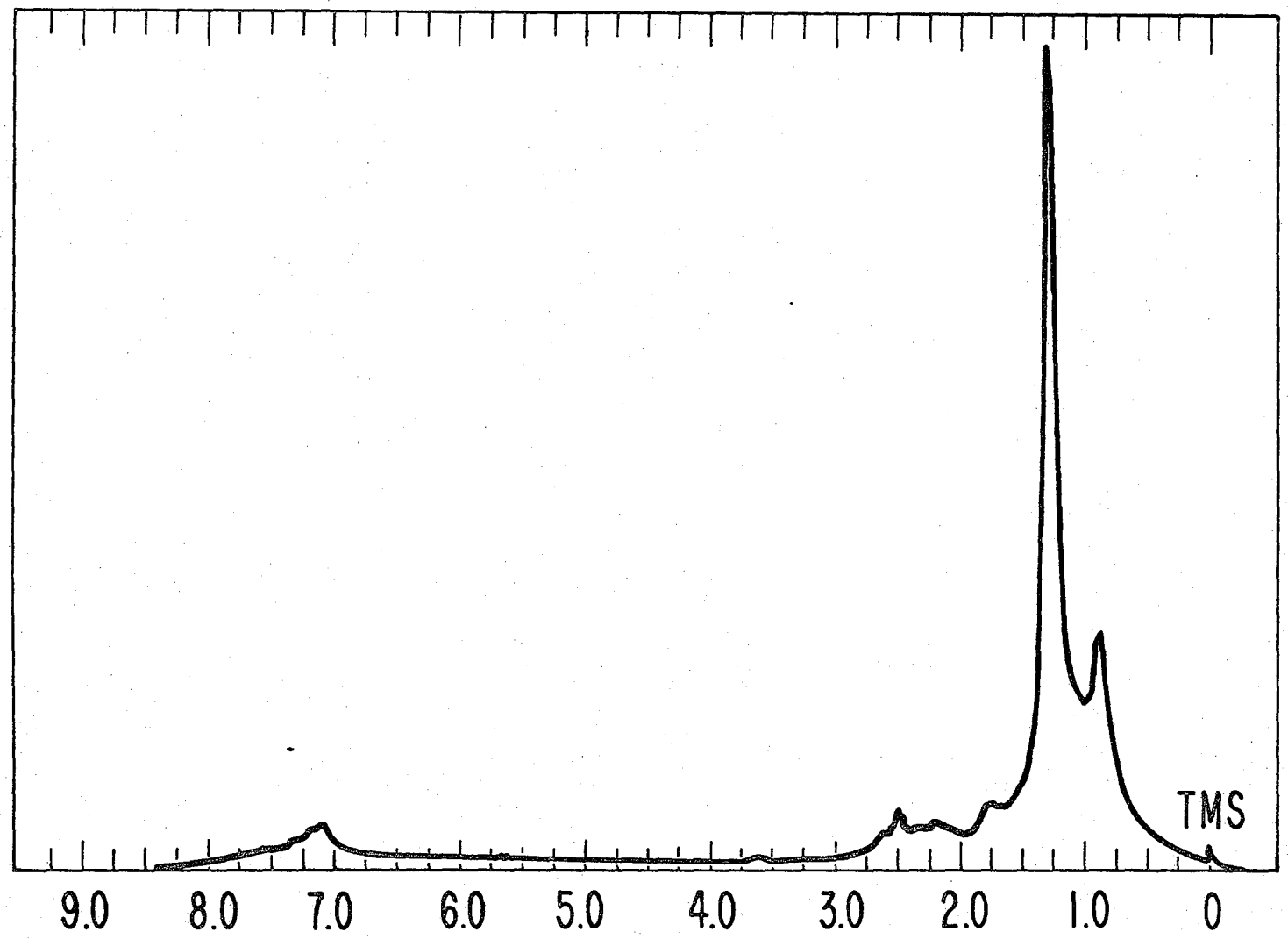


Fig. 14. ^{1}H-NMR spectrum (in d_5-pyridine) of the material extracted from Roland seam coal using tetralin at 250°C for 4 hr.

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the quinoline extract approximately 60% soluble in d_5-pyridine at room temperature. The spectrum of the d_5-pyridine used in this study is presented in Fig. 15. The amplitude setting was higher than the settings used for the spectra of the extracted material. Therefore, the spectra of the extracted material are reasonably free from peaks due to impurities in the d_5-pyridine.

Each of the spectra was divided into the previously described regions of Harom, Halpha, Hbeta, and Hgamma according to the method of Anderson.[47] The peak areas within each region were evaluated in order to calculate the approximate relative amounts of aromatic, and alpha, beta, and gamma aliphatic protons. There are two strong peaks which are characteristic of each spectrum. One peak is located in the Hbeta region at approximately 1.30 ppm.* The fact that the peak is so strong and sharp indicates that there are many protons in roughly the same chemical environment. This is true of normal saturated hydrocarbons that are expected to be present in the material extracted by each of the four contacting solvents. The other peak characteristic of each spectrum is located at about 0.9 ppm in the Hgamma region on the shoulder of the large Hbeta peak. This peak represents methyl groups beta or further from an aromatic nucleus or (more likely) methyl groups on the saturated hydrocarbons.

The data in Table V summarize the relative proton distributions of the material extracted by each of the four contacting solvents. Although the derived proton distributions are only approximate, some

*A downfield shift of 180 Hz from tetramethylsilane equals 1 ppm.

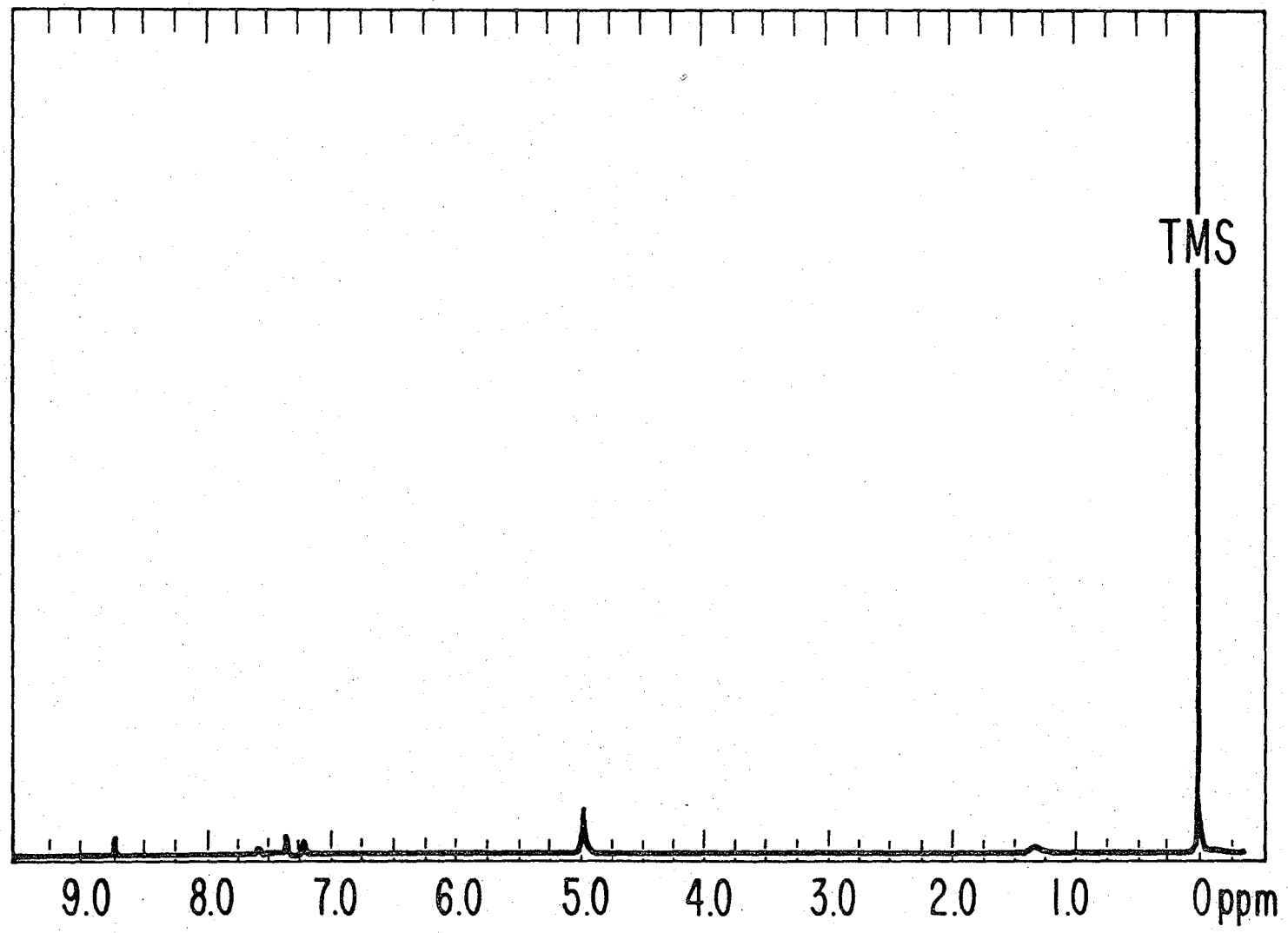

Fig. 15. ^{1}H-NMR spectrum of d_5-pyridine NMR solvents.

XBL779-1865

Table V. Proton distributions of the material extracted by quinoline, piperidine, ethylenediamine, and tetralin at 250°C from Roland seam coal.

Extract	Harom 6.00 to 8.67 ppm*	Halpha 2.00 to 3.33 ppm*	Hbeta 1.00 to 2.00 ppm*	Hgamma 0.50 to 1.00 ppm*
Quinoline	12.9	12.4	60.4	14.3
Piperidine	3.8	24.0	61.8	10.4
Ethylenediamine	21.4	31.0	38.5	9.1
Tetralin	7.6	9.5	60.9	22.0

*A downfield shift of 180 Hz from tetramethylsilane equals 1 ppm.

general statements may be made concerning the chemistry of each of the four extracts.

The spectrum of quinoline extract displays an even distribution between aromatic and alpha protons. This suggests an aromatic character of the extract with some degree of substitution. The size and shape of the Hbeta region is similar to that of the other extracts. The peak at 0.90 ppm in the Hgamma region is sharper than in some of the coal extracts. This may indicate a more uniform chemical environment for these protons as with methyl groups on saturated hydrocarbons. The small hump at 5.0 ppm is probably a water resonance.[56]

Piperidine extract displays the same strong peaks in the Hbeta and the Hgamma regions as so the extracts of the other solvets. As mentioned before, the strong Hbeta peak is probably due to the presence of normal alkanes. The fact that the distribution of protons in the Harom region is only 3.8% does not suggest that the extract is only 3.8% aromatic by nature. The relatively high yield of 35.4% and low molecular H/C ratio of 0.906 indicate that more aromatics must be present. These rings may be condensed or highly substituted and, therefore, not have a large number of aromatic protons. The idea of highly substituted aromatics is suggested by the relatively high Halpha distribution. In fact, unless the alpha substitution were limited to methyl groups, some of the Hbeta protons may be attributed to protons on carbons beta to an aromatic ring. The Hgamma protons are attributed to methyl groups on saturated compounds or positioned gamma to an aromatic.

Although ethylenediamine extract was the least soluble in d_5-pyridine, it gave the broadest distribution of protons. The large amount of aromatic protons verifies the presence of aromatic structures expected from the 64.3% yield and small H/C ratio (0.458) of the extracted material. Substitution of the rings is suggested by the significant Halpha and Hbeta fractions. However, the sharp peak at 1.30 ppm shared by the spectra of the rest of the extracts probably indicates the presence of normal paraffin chains. The significant amount of proton resonance from 3.33 to 6.00 ppm is not accounted for in the distribution of protons proposed by Anderson.[47] Absorption from 3 to 5 ppm is characteristic of methyl, methylene, or methine protons that are adjacent to nitrogen or oxygen atoms of amides, amines, esters, or other groups.[57] Peaks in this region could represent chemically combined ethylenediamine or piperidine in their respective spectra.

The distribution of protons in the material extracted by tetralin is similar is some way to that for quinoline. The small amount of aromatic protons may indicate highly substituted aromatics, condensed hydroaromatic rings, or simply a small amount of aromatics in the extract. At only an 8.02% yield of extraced material, a great quantity of aromatic species would not be expected. The sharp, narrow peak at 1.30 ppm with its sharp shoulder may be due to normal paraffins and methyl groups on saturated hydrocarbons. The peak at 2.60 ppm is characteristic of alpha methylene protons on the hydroaromatic ring of tetralin, however, the a aromatic portion does not lie in the expected (6.85) region for tetralin.[58]

IV. CONCLUSIONS

The results of this investigation are consistent with an anticipated high degree of activity of specific solvents with low rank coals. The interaction of these solvents with a western subbituminous coal indicates a number of behavioral patterns of this coal which may be of importance in the conversion of western coals into liquid products.

1. A large fraction of the subbituminous coal can be dissolved with strong organic amine bases below the coal pyrolysis temperature (325°C), and the dissolution is usually accompanied by a large amount of retained solvent in the extract. This behavior and the small hydrogen to carbon ratios in the dissolved material indicate that strong specific interactions occur between these amines and portions of the coal structure.

2. Elemental balances suggested a deficiency of hydrogen in the extract and residual coal, usually greater in the case of more severe contacting conditions. The formation of amides with primary and secondary amine solvents provides a reasonable explanation for part of the discrepancy in that water is evolved as the amide co-product.

3. Proton nuclear magnetic resonance studies on material extracted by quinoline, piperidine, ethylenediamine, and tetralin indicate that generally a much larger fraction of this material may be in the form of aliphatic or saturated hydrocarbons than in aromatic structures. The fact that ^{1}H-NMR is limited to characterizing the chemical environment of protons, however, must be remembered in making this observation. More conclusive evidence may be provided from ^{13}C-NMR, where the chemical environments of the carbon atoms are studied.

The results of this investigation indicate other possible areas of further study including the nature of the interactions between organic amine bases and subbituminous coal. Since these solvents seem particularly effective in dissolving a subbituminous coal under mild conditions, an incentive exists to obtain a more complete understanding of the relevant chemical and physical processes in these interactions. Of particular interest are the processes associated with the apparent loss of hydrogen and incorporation of contacting solvent. Additional characterization of the extraction products, including product gases, may provide necessary information in this area.

The use of a mixed solvent system, which combines solvents differing in the source of their chemical activity with respect to coal, is another interesting area for study. One such combination is that of a hydrogen donor and a specific solvent. The interaction of a strong specific solvent with subbituminous coal may produce active sites in the coal structure that could then be hydrogenated by a hydrogen donor solvent. In this way hydrogen transfer could be accomplished below coal pyrolysis temperatures.

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APPENDIX A. INCORPORATION OF SOLVENT IN EXTRACTION PRODUCTS

The incorporation or retention of solvent in either the extracted material or the residual coal solids has been reported in many systems of coal/solvent contacting by several authors.[1,8,14,28,35] Solvent incorporation is most apparent in reactive or specific solvent systems since the solvent power of the organic liquid lies in its ability to chemically interact with structural features of the coal. The occurrence of solvent retention is easily recognized by the observation that the sum of the weights of the residual coal and extracted material is greater than the weight of the coal originally charged to the coal/solvent contacting system. In the case of nitrogen-containing solvents, such as amines, solvent incorporation is detected by the presence of nitrogen in excess of that in the original coal. Various procedures attempting to remove incorporated amines have been investigated such as precipitating the extract from solution with another organic liquid, drying the extract for extended periods of time under reduced pressure, or precipitating the extract from acidified aqueous solutions.[35] However, since the contacting solvent is chemically bound to the extracted species, these procedures are not successful in removing the combined amines.

The presence of retained solvent affects the elemental carbon and hydrogen composition of the extract and residue as well as the yield of extracted material. For this reason, the elemental analyses for the carbon and hydrogen and the yield of extracted material have been corrected for the effect of retained solvent. The basic assumption necessary for making the corrections is that the nitrogen from the coal is distributed evenly between the extracted material and the

residual coal. Even if this is not true, the error in the correction will be small since the subbituminous coal used in this investigation has only 0.97 wt% nitrogen. The corrections are based on the solvent molecule being retained as a unit without losing any of its atoms in the process of chemical combination. As will be discussed, this is not necessarily the true situation.

A nitrogen balance on the extracted material gives:

$$N_o = \frac{0.0097\ W_{E*} + N_s W_s}{W_{E*} + W_s} \qquad \text{(A-1)}$$

where 0.0097 is the weight fraction of nitrogen in the original coal; W_{E*} is the weight of the solvent-free extract; N_s is the weight fraction of nitrogen in the solvent; W_s is the weight of solvent in the extracted material; and N_o is the observed weight fraction of nitrogen in the extract. If we let $S = \frac{W_s}{W_{E*}}$, that is, the weight ratio of solvent to solvent-free extract, we can restate Eq. (A-1) as:

$$S = \frac{N_o - 0.0097}{N_s - N_o} \qquad \text{(A-2)}$$

The yield of extracted material is then simply corrected using Eq. (A-2) and the relationship:

$$E^* = E - E^* S \qquad \text{(A-3)}$$

where E^* is the yield (weight fraction) of the solvent-free extract from the original dry, ash-free coal; and E is the yield of solvent-combined extract.

The corrections for the elemental hydrogen and carbon analyses are based on the fact that the observed hydrogen or carbon (H_o or C_o) in the extract (or residue) is the sum of the hydrogen (or carbon)

contributed by the extracted material and the hydrogen (or carbon) present from the amine solvent. For hydrogen:

$$H_o = \frac{H^*W_{E^*} + H_sW_s}{W_{E^*} + W_s} \qquad \text{(A-4)}$$

where H^* is the weight fraction of hydrogen in the solvent-free extract; and H_s is the weight fraction of hydrogen in the solvent. This gives:

$$H^* = H_o(1 + S) - H_sS \qquad \text{(A-5)}$$

The C^* is the weight fraction of carbon in the solvent-free extract; and C_s is the weight fraction of carbon in the solvent.

Table A-1 presents the observed, uncorrected elemental analyses of the residues and the extracts from all the coal/solvent contacting experiments. Also included are the yield of residual coal (dry basis) and the yield of extracted material (dry basis). These yields do not add to 100% because of the retention of contacting solvent in both the extract and residue.

The elemental nitrogen compositions in Table A-1 of the extracts from the 200°C and two 250°C quinoline extractions were not those used to calculate the solvent-free yield of extracted material and the amount of retained solvent in the solvent-combined extract. The data in Table A-1 were determined later when the originally observed elemental compositions became questionable. Both sets of data follow.

Table A-1. Summary of Data Resulting from the Extraction of Roland Seam Coal with Pyridine, Quinoline, Piperidine, Ethylenediamine, Tetrahydrofuran, or Ethanolamine for 4 Hours.

Conditions		Residue			Extract			Extract Yield (% Dry Coal)	Residue Yield (% Dry Coal)
Solvent	Temp. (°C)	%H	%C	%N	%H	%C	%N		
Pyridine	100	4.45	50.87	0.94	8.50	75.98	0.97	8.0	86.1
Pyridine	150	4.60	55.20	1.0	8.54	76.36	0.81	8.8	89.7
Pyridine	200	4.30	52.90	1.2	8.00	76.04	0.88	11.1	87.6
Pyridine	200	4.30	58.00	1.4	8.48	76.65	1.07	11.6	87.8
Pyridine	250	4.10	53.40	1.6	7.29	73.99	1.48	14.5	85.2
Pyridine	250	3.90	51.80	1.4	8.15	75.95	1.13	13.6	83.8
Pyridine	300	3.87	61.29	1.63	8.05	77.63	1.24	17.2	78.3
Pyridine	300	3.70	59.40	1.60	7.24	76.20	1.50	18.4	74.6
Pyridine	250				7.71	73.43	1.67	15.5	
do. (24 hr)					7.09	72.26	2.03	21.1	
do. (48 hr)					7.23	74.04	1.83	21.9	
do. (72 hr)					6.83	72.50	2.05	25.0	
do. (100 hr)		3.60	56.70	1.70	7.34	76.33	1.48	21.3	74.7
Quinoline	200	3.60	58.50	1.80	6.03	73.03	3.61	15.9	86.6
Quinoline	250	3.30	58.10	1.80	5.37	71.08	4.29	27.3	79.6
Quinoline	250	3.20	54.60	1.85	4.83	69.76	4.78	38.0	82.8
Quinoline	300	3.05	59.30	2.20	4.96	71.61	3.62	35.2	70.5
Quinoline	350	2.90	60.60	3.10	4.95	79.24	5.36	44.9	66.9
Quinoline	350	3.22	61.76	3.36	5.17	81.32	5.89	54.7	66.1
Piperidine	105	5.40	61.10	3.40	8.84	74.66	3.93	7.9	99.7
Piperidine	150	4.87	62.20	3.87	9.17	75.79	5.94	10.7	88.5
Piperidine	200	5.01	59.97	3.46	8.09	74.06	5.21	22.0	92.2
Piperidine	250	5.10	59.90	3.90	8.55	75.40	6.78	48.0	81.5
Piperidine	250				8.43	74.97	6.70	32.9	
do. (24 hr)					8.73	75.83	7.63	105.0	
do. (48 hr)		5.19	54.48	4.12	8.67	75.36	7.80	76.1	67.8
Ethylenediamine	150	4.70	57.0	7.10	6.71	61.17	18.33	58.0	70.4
Ethylenediamine	200	4.20	51.0	7.50	7.03	62.02	17.60	64.0	63.8
Ethylenediamine	250	3.60	50.0	8.50	6.85	69.15	17.25	84.8	47.5
Tetrahydrofuran	150	4.90	61.80	1.10	9.90	78.54	0.47		
Tetrahydrofuran	200	4.50	53.40	0.90	9.28	77.61	0.46		
Tetrahydrofuran	200	4.53	55.91	0.91	9.67	78.20	0.61		
Ethanolamine	150	5.31	52.84	4.91	6.73	55.16	14.34	101.4	63.1
Ethanolamine	250	--	--	--	--	--	--	202.0	22.4

0 0 0 0 4 8 0 0 6 6 5

Quinoline Extraction Temperature (°C)	Original %C	Original %H	Original %N	Replicate %C	Replicate %H	Replicate %N
200	65.46	4.86	2.93	73.03	6.03	3.61
250	64.43	4.77	3.17	71.08	5.37	4.29
250	62.60	4.57	4.15	69.76	4.83	4.78

The original nitrogen analyses were applied for the correction of the yield of extract and the amount of extract solvent retention since they were measured of the extract sample used to calculate the yield of dissolved coal.

The proper correction of the extract or residue for the incorporation of contacting solvent depends on the form in which the incorporated solvent exists. If the solvent molecule loses any of its atoms in the process of chemical combination, the methods described here will give an improper correction for solvent incorporation. Carbon is probably not cleaved from the molecules of any of the solvents used in this investigation under these contacting conditions. This is reflected by the relatively good mass balances on carbon. Hydrogen, however, is easily lost through reactions such as amide formation and hydrogen transfer. The elemental balances on hydrogen show a general loss of hydrogen. The results of adjusting Eq. (A-5) for the loss of hydrogen has been discussed (see Chapter III).

APPENDIX B. PRODUCT GAS ANALYSES

The quantity and the composition of the gases resulting from coal/solvent interactions were studied using mass spectroscopy for selected contacting experiments. The collected well-mixed gas sample was first separated into three fractions in order to remove the helium used to pressurize coal/solvent contacting apparatus. The number of moles of helium and of the gases in the three fractions were calculated, assuming ideal gas behavior, from the measured pressure, volume, and temperature of each fraction. These fractions were analyzed separately by mass spectroscopy for their respective compositions, and the mole fraction of each gaseous component was calculated from its relative peak height in the mass spectrum. From these data, the number of molecules of each gas produced from the coal/solvent contacting experiment were calculated knowing the pressure, volume, and temperature of the gases at the time of sampling and assuming ideal gas behavior. The quantity of each gas is reported as a wt% of the total weight of product gases. The yield of product gas is simply the ratio of the total weight of product gas to the dry, ash-free weight of original coal.

This method of gas analysis was checked by introducing measured amounts of known gases into a sample of pure helium and conducting the indicated separations and mass spectral analyses. Each component was added to an evacuated 500 ml sample bulb through a mercury covered fritted disk using a mercury displacement gas pipette of constant volume. Helium was then added to 1 atmosphere. The results in Table B-1 indicate that quantitative recovery of the components

added to helium is possible using the method of gas analysis described in this investigation. The amounts of methane and carbon dioxide added to the sample are unknown, because poor contact between the pipette and the fritted disk resulted in the loss of part of the sample. In these cases, another pipette-full of the gas sample was introduced.

In addition to product gases, each gas sample contained a certain amount of nitrogen, oxygen, and argon which was from the presence of air. A small amount of air was expected because of the inability to completely degas the solvent or totally evacuate the contacting apparatus. The amount of air was calculated, on the basis of argon composition, assuming air consists of 78.08 mole% N_2, 20.95% O_2, 0.0093% Ar, and 0.0003% CO_2. The results of this calculation usually indicated a concentration of oxygen in the gas sample that was lower than that expected for the included for air; the nitrogen concentration was slightly higher than that expected. This is probably due to some oxidation of the coal or solvent and a lack of precision in calculating air on the basis of the extremely small quantities of argon present in the gas sample. The raw data from the gas analyses, not corrected for air, are summarized in Table B-2.

Table B-2. Product gas analysis for contacting Roland seam coal with pyridine, quinoline, piperidine, and tetrahydrofuran for 4 hr.

Component (in wt%)	Quinoline 350°C	Pyridine 300°C	Piperidine 250°C	Tetrahydrofuran 200°C
CO_2	69.2	87.2	0.0	66.8
CO	16.2	8.20	0.0	8.09
CH_4	6.38	0.942	0.08	0.24
H_2	0.051	trace	0.01	0.02
NH_3	0.0	0.0	3.20	0.0
H_2O	3.32	0.0	0.0	0.0
N_2	4.30	2.97	85.4	21.7
O_2	0.50	0.598	10.1	2.77
Ar	0.034	0.0601	1.20	0.36
Total Mass (grams)	2.9191	0.5638	1.4552	0.1224

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APPENDIX C. INCORPORATION OF SOLVENT IN COAL EXTRACT FRACTIONS

Elemental nitrogen analyses suggest that portions of the chemically combined contacting solvent are contained in the oil, asphaltene, and preasphaltene fractions of the original coal extract. Therefore, it is necessary to correct the yield and the elemental composition of each fraction according to the amount of retained solvent indicated by its elemental nitrogen analysis. If it is assumed that cyclohexane, benzene, and pyridine are not incorporated in their respective soluble fractions, then no change is necessary in the method for the correction of the observed elemental hydrogen and carbon compositions presented in Appendix A. This assumption is made since incorporation of these solvents is unlikely and no method is readily available for determining their presence in the dissolved material. On this basis, a similar equation to the one in Appendix A for the solvent-free yield of extracted material may be derived for the solvent-free yield of each fraction on the original amount of dry ash-free coal:

$$F^* = \left(\frac{W_F - W_{F^*}S_F}{W_e - W_{e^*}S_e}\right) E^* \qquad \text{(C-1)}$$

where W_F is the observed weight of the fraction (oil, asphaltene, or preasphaltene); W_{F^*} is the weight of the fraction corrected for the weight of retained solvent; $S_F = W_s/W_{F^*}$ is the weight ratio of solvent to solvent-free extract in the fraction; E^* is the yield (weight fraction) of the solvent-free extract from the original dry ash-free coal; W_e is the observed weight of the coal extract to be separated into fractions; W_{e^*} is the weight of the coal extract

corrected for the weight of retained solvent; $S_e = W_s/W_{e^*}$ is the weight ratio of solvent to total solvent-free extract; and F^* is the yield of a fraction on a dry, solvent and ash-free basis.

The uncorrected yield of each fraction as well as the observed, uncorrected elemental analyses for hydrogen, carbon, and nitrogen are presented in Table C-1.

The results of the separation of the material extracted in the "Pyridine-B" run in Table C-1 have not been considered further in this study because the extract was believed to contain portions of undissolved residual coal. This sample was obtained from a contacting experiment conducted early in this investigation when the solution of extracted material in contacting solvent was not properly filtered.

Table C-1. Summary of Uncorrected Data from Separation of Pyridine, Quinoline, Piperdine, and Ethylenediamine Coal Extracts into Oil, Asphaltene, Preasphaltene, and Pyridine Insoluble Fractions.

Solvent (°C)	Extract				Oils				Asphaltenes				Preasphaltenes				Pyridine-insol.
	% DAF	%H	%C	%N	% DAF	%H	%C	%N	% DAF	%H	%C	%N	% DAF	%H	%C	%N	% DAF
Pyridine (150°C)	10.4	8.54	76.36	0.81	4.19	11.24	79.58	0.19	1.14	7.97	76.12	0.86	5.07	6.21	71.82	2.19	--
Pyridine (200°C)	13.8	8.48	76.65	1.07	5.17	11.31	79.48	0.20	1.42	8.02	75.56	0.98	7.22	6.21	72.41	2.13	--
Pyridine-A (250°C)	16.0	8.15	75.79	1.13	5.92	11.17	79.90	0.28	1.90	8.05	73.66	1.03	8.18	6.25	71.95	2.10	--
Pyridine-A (250°C)	do.	do.	do.	do.	5.06	--	--	--	1.85	--	--	--	9.08	--	--	--	--
Pyridine-B (250°C)	17.1	7.29	73.99	1.48	3.28	11.52	79.77	0.16	1.61	8.34	76.40	0.84	12.2	5.99	71.79	2.13	--
Pyridine-B (250°C)	do.	do.	do.	do.	3.29	--	--	--	1.87	--	--	--	11.9	--	--	--	--
Pyridine (300°C)	21.7	7.24	76.20	1.50	4.99	10.79	77.82	0.24	3.13	7.13	73.74	1.26	13.6	6.01	74.44	1.95	--
Quinoline (250°C)	32.2	5.37	71.08	4.29	5.73	8.98	82.49	3.68	3.60	7.28	76.70	4.07	22.5	5.41	68.08	4.06	0.37
Piperidine (250°C)	56.7	8.55	75.40	6.78	17.6	10.17	77.10	8.13	16.8	8.36	75.09	8.37	22.0	7.47	73.60	8.35	0.39
Ethylenediamine (250°C)	100	6.85	69.15	17.25	0.0	--	--	--	0.0	--	--	--	45.1	6.12	63.06	20.83	55.2

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