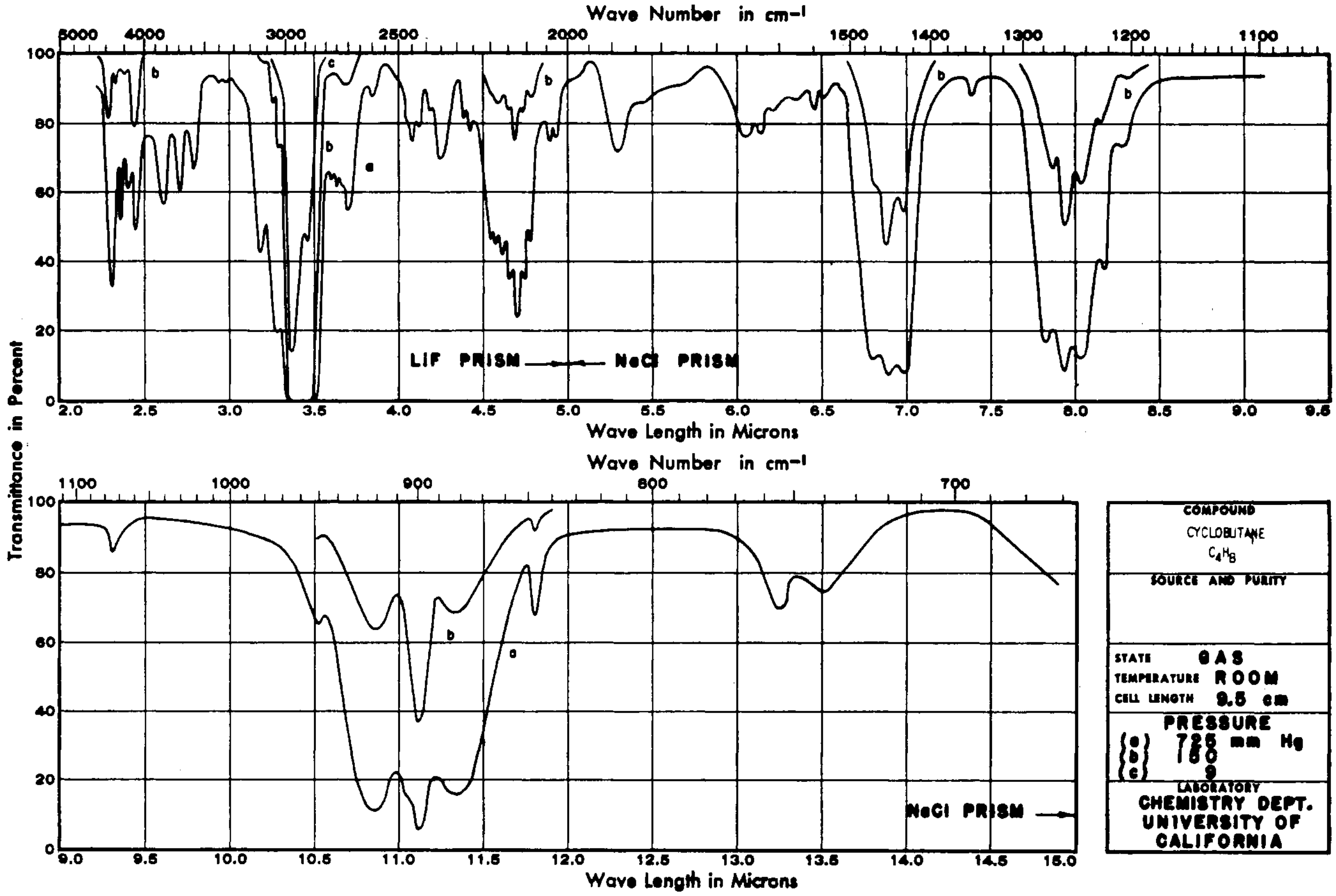

Figure 5. Infrared spectrum of cyclobutane

ACKNOWLEDGMENT

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Source and Some General Properties of Humic Acids from Lignitic Materials

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The lignite beds of North Dakota, South Dakota, and Montana contain numerous deposits of a poorly consolidated material, locally called leonardite, which is somewhat richer in oxygen and alkali-soluble, acid-insoluble components than is the average lignite. Although leonardite has some commercial value as an ingredient of drilling muds and as a soil conditioner, more important uses might be found for the recovered alkali-soluble portion as ion exchangers (*4, 17*) and as a source of chemicals (*9, 12*) and industrial carbon. Further, leonardite probably represents a naturally oxidized lignite (*18*) and might well be a logical starting point for an examination into the chemical nature of fossil fuels, since the products of coal oxidation, usually referred to as "humic acids," represent in the minds of many investigators (*1-3, 5, 6,* p. 404; *10-12, 15, 19, 21, 24*) minor degradation of the macromolecule to give material in part amenable to characterization by classical procedures. There is also strong evidence to support the theory that natural humic acids, which in general closely resemble the artificial product, are the precursors of some, if not all, coals (*7, 13, 14, 16, 22, 23*).

Lavine (*18*), in collaboration with Mason, studied the yields of humic acids from North Dakota lignite and found that maximum yield of extracted material was obtained with sodium hydroxide solutions of 2 to 4% and that increasing the extraction temperature increased the yield of extracted material. The purpose of this investigation was to determine the amounts and the general characteristics of humic acids recoverable from lignite and oxidized lignites or leonardites, and to investigate methods for their purification.

EXPERIMENTAL

Preparation of Samples. The lignite, "slack seam" (a shallow-lying bed of poorly consolidated lignite above the seam regularly mined which is removed during operations to recover the deeper coal), and leonardite used in this study were portions of those materials gathered for previous carbonization studies. They are designated as Baukol-Noonan face (30-foot overburden), Baukol-Noonan from slack seam, and Peerless leonardite face, respectively. Properties of the lignites are shown in Table I. The samples were collected from the face of the seam indicated by first hand-chipping to expose a fresh surface and then cutting out a column of such dimension as to provide approximately 150 pounds of lignite when the entire column had been removed. Samples were crushed to −⅛-inch, and portions of each of the lignites were air-dried. A portion of the leonardite was dried in an oven at 105° C. for 60 hours and then pulverized. All samples were stored in airtight containers.

Table I. Properties of Lignites
(Per Cent)

	Baukol-Noonan Lignite	Baukol-Noonan Slack Seam	Leonardite
Proximate analysis of lignite as received			
Moisture	36.2	42.6	53.4
Volatile matter	26.4	26.4	23.9
Fixed carbon	31.0	22.6	15.0
Ash	6.4	8.4	7.7
Proximate analysis of lignite[a]			
Volatile matter	46.1	53.9	61.4
Fixed carbon	53.9	46.1	39.6
Ultimate analysis of lignite[a]			
Hydrogen	5.1	3.7	4.0
Carbon	73.8	65.7	63.9
Nitrogen	1.2	1.3	1.2
Oxygen[b]	19.9	28.4	28.4
Sulfur	1.0	0.9	2.5

[a] Moisture- and ash-free.
[b] By difference.

Preliminary Experiments. Several preliminary experiments were made to determine the factors that affect the ash content of recovered humic acids.

To test the effect of preliminary washing of the leonardite, one 20-gram sample of oven-dried leonardite was stirred 30 minutes with 200 ml. of boiling 0.02*N* hydrochloric acid (I) and a second 20-gram sample stirred 30 minutes with 200 ml. of boiling 1*N* hydrochloric acid (II). The mixtures were then filtered by suction, washed with hot water, and dried. Ten-gram portions of each of the dried residues, along with two 10-gram samples (III) of the original dried leonardite, were each stirred 30 minutes at room temperature with 500 ml. of 0.3*N* ammonium hydroxide and the mixtures allowed to stand overnight before centrifuging to remove the insoluble material. Ten milliliters of concentrated hydrochloric acid was then added to each of the humate solutions to precipitate the humic acids, which were recovered by centrifuging. Acid recovered from one 10-gram sample of the original leonardite (III) was resuspended in water by stirring and again recovered by centrifuging (IV). All samples of recovered humic acids were then dried overnight at 105° C.

Results of ash determinations on these samples of acids are (weight per cent) III, 3.7; IV, 1.3; I, 3.4; II, 0.7.

Dried humic acids recovered from untreated leonardite by room-temperature extraction with 1*N* sodium hydroxide and having an ash content of 4.8% were variously treated as follows:

A 10-gram portion was boiled 30 minutes in 500 ml. of water containing a few drops of hydrochloric acid (V). The mixture was then filtered by suction. A second 10-gram portion was dissolved in 500 ml. of 0.1*N* ammonium hydroxide, reprecipitated with concentrated hydrochloric acid, and recovered by centrifuging (VI) A third 10-gram portion was stirred for 15 minutes at room temperature with 250 ml. of 5*N* hydrochloric acid, the mixture filtered, and the residue washed with 250 ml. of hot water (VII). A fourth 10-gram portion was boiled 15 minutes with 100 ml. of 5*N* hydrochloric acid; the mixture was then allowed to cool and stand 15 hours at room temperature before filtering. The residue was washed with 250 ml. of water. The dried acids were then mixed with 10 ml. of concentrated hydrochloric acid, and the mixture was warmed on a steam bath. One hundred milliliters of water was added, the mixture filtered, and the residue washed with 250 ml. of water (VIII). The purified acids from each treatment were dried in an oven at 105° C. Ash contents of the purified acids are, (weight per cent) V, 2.1; VI, 1.3; VII, 0.8; VIII, 0.4; original humic acids, 4.8.

To determine the effect of the concentration of humic acids in the extracting solution on the ash content of recovered humic acids, 10 grams of oven-dried and pulverized leonardite was added to each of four beakers containing 250, 400, 500, and 1000 ml. of water, respectively. Ten milliliters of concentrated ammonium hydroxide was added to each beaker and the mixtures were stirred 30 minutes at room temperature. The mixtures were allowed to stand at room temperature for 16 hours before centrifuging to remove the insoluble material. Ten milliliters of concentrated hydrochloric acid was added to each of the humate solutions to precipitate the humic acids. The precipitated acids were recovered by centrifuging and dried at 105° C.

The effect of the concentration on ash contents of the recovered humic acids is shown graphically in Figure 1. At the higher concentrations the solution becomes so viscous that separation of the mineral matter is extremely difficult.

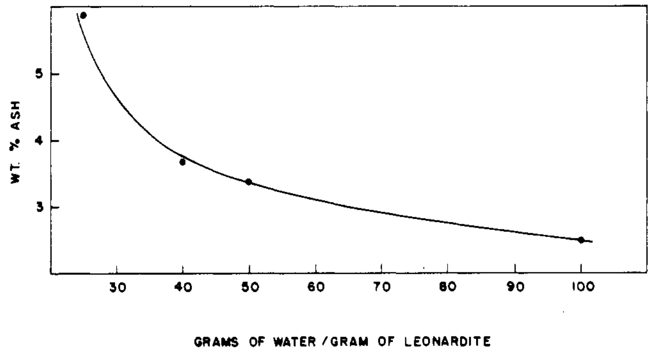

Figure 1. Effect of dilution on ash content of recovered humic acids

Alkaline Extraction of Lignites. Forty-gram samples of the air-dried lignites were stirred 90 minutes at room temperature with 500 ml. each of 1*N* solutions of various alkalies. Each mixture was allowed to stand 15 hours at room temperature and then stirred an additional 30 minutes before centrifuging to remove the insoluble material. The insoluble material was thoroughly washed with water, and the washings were added to the humate solution. After adjustment of the pH of the humate solution to approximately 2 with concentrated hydrochloric acid, the precipitated humic acids were removed by centrifuging and dried overnight at 105° C. The dried acids were washed twice with 500 ml. of water containing a few drops of hydrochloric acid and redried.

Properties of the recovered humic acids and yields from each of the various lignites are shown in Table II. The humic acids

Table II. Yields and Properties of Humic Acids from Lignitic Materials

	Lignite Slack		Leonardite			
Extraction mediums	1N NaOH	1N NaOH	1N NaOH	Sat. $Ca(OH)_2$	1N NH_4OH	1N Na_2CO_3
Humic acids, wt. %[a]	5.0	86.2	84.1	Tr.	77.8	84.1
Analysis, m.a.f. %						
Volatile matter		50.0	50.0		50.0	50.6
Fixed carbon		50.0	50.0		50.0	49.4
Hydrogen		3.5	3.5		3.4	3.4
Carbon		64.2	63.5		62.7	63.5
Nitrogen		1.3	1.3		1.7	1.3
Oxygen[b]		30.4	31.1		31.5	31.1
Sulfur		0.6	0.7		0.7	0.7
Ash, %		3.7	3.9		1.8	3.1

[a] $\frac{\text{Wt. of humic acids, m.a.f.}}{\text{Wt. of lignitic material, m.a.f.}} \times 100.$

[b] By difference.

obtained from lignite by extraction with 1N alkali solutions show similar properties and agree with the values for the humic acids obtained by oxidation of bituminous coal (*1*, *15*, *19*). Properties of the humic acids from air-dried lignite by extraction with 1N sodium hydroxide and from air-dried leonardite by extraction with calcium hydroxide were not determined because of the small yields obtained.

Bulk Extraction of Humic Acids. Fifteen hundred grams of undried leonardite was digested with 4000 ml. of 2.5N sodium hydroxide solution for 8 hours on a steam bath, and the mixture allowed to cool and stand overnight. Insoluble material was separated by centrifuging and washed twice with water, the washings being added to the humate solution. Sulfuric acid was added to the humate solution to adjust the pH to 3 and precipitate the humic acids, which were recovered by centrifuging, dried at 105° C., washed thoroughly with water, and redried. A portion of the bulk acids was treated with hot 5N hydrochloric acid, followed by cold, concentrated hydrochloric acid, as in method IV above.

Analyses of the bulk and purified acids are shown in Table III.

A slightly higher carbon and hydrogen content and a lower oxygen content indicate that the humic acids obtained through extraction with hot 2.5N alkali solution are somewhat different than those obtained with cold, more dilute alkali, possibly because of the presence of "humins" (*6*, p. 162). It is also evident that the rigorous purification methods alter the composition of the humic acids.

DISCUSSION

A large part of the ash in the recovered humic acids results from the inorganic salts formed in neutralizing the extraction base, most of which can be removed by thorough washing with water containing a small amount of acid to prevent peptizing of the humic acids. The ash content may be lowered somewhat further by treatment with relatively strong acid. When ammonium hydroxide was used as the extracting base, the ash value was somewhat lower, probably because of volatilization of part of the ammonium chloride formed during neutralization, since the increased nitrogen content of the humic acid sample indicates that an ammonium salt was present.

Table III. Ultimate Analysis of Bulk and Purified Humic Acids
(Per Cent)

	Bulk Acids	Purified Acids
Ash	1.0	0.2
Hydrogen	4.3	3.5
Carbon	67.5	60.9
Nitrogen	1.3	1.2
Oxygen[a]	26.0	33.2
Sulfur	0.9	0.8

[a] By difference.

There is strong evidence that the humic acids in leonardite are present as the calcium salts. Thus, only a trace of humic acids can be recovered by treatment with calcium hydroxide solution (pH 12.4), although sodium carbonate (pH 11.6) is as effective as sodium hydroxide solution in dissolving the humic acids in leonardite. The calcium salts of the humic acids are virtually insoluble in water, while the ammonium salt and the sodium salt are very soluble. Essentially complete solution of the recovered humic acids in a 3 to 1 acetone-water solution can be achieved in a few minutes, whereas less than 3% of the original leonardite can be dissolved in the same solvent, even after prolonged contact, and calcium ion will precipitate humic acids from the acetone-water solution. In contrast, Polansky and Kinney found humic acids from bituminous coal, which had been treated with nitric acid, to be readily soluble in acetone-water mixtures (*20*). Preliminary treatment of the leonardite with very dilute acid sharply increases the solubility of the humic acids in acetone-water solution.

The sulfur and nitrogen contents of the recovered humic acids are remarkably similar, regardless of the ash content, and indicate that these elements form an integral part of the humic acid molecule. The slightly higher sulfur content present when sulfuric acid is used as a precipitating acid may be accounted for by the presence of the sulfate salt, just as the nitrogen content is higher when ammonium hydroxide is used as the extracting base. Kreulen (*16*) reported examination of Rosa coal that contains more than 10% organically combined sulfur, and on oxidation produces humic acids with 8% sulfur. Results indicated that the sulfur partly replaces oxygen and that an essential portion is present in ring structures. Higuchi and Tsuyuguchi (*8*) included nitrogen in their molecular formula for humic acid extracted from Nakayama lignite.

CONCLUSIONS

Both leonardite and slack-seam lignites appear to be excellent sources of humic acids, with as much as 86% of the lignite material soluble in alkali. Yields and properties of the acids compare favorably with the values obtained through oxidation of bituminous coal. Ultimate analyses and humic acid content of slack and leonardite indicate that they are similar, although there are differences in the proximate analyses.

Recovered humic acids may be purified sufficiently for most purposes by simple water washing or by a light acid treatment. Humic acids with a very low ash content may be produced by treatment with strong acids. The ultimate composition of the humic acids is, however, altered somewhat by the severe treatment required.

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Viscosity of Helium, Oxygen, Helium-Oxygen, Helium-Steam, and Oxygen-Steam Mixtures at High Temperatures and Pressures

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The need for the viscosity of gases arises in at least three important phases of chemical engineering: fluid mechanics, heat transfer, and kinetics. Because the experimental determination of the viscosity of a gas is difficult and expensive, the practicing engineer must usually obtain the viscosity data he needs from the published literature. The viscosity of pure component gases at atmospheric pressure is readily available in the literature over wide temperature ranges. In addition to the pure component data, several charts and nomographs may be used to obtain a reliable estimate of the viscosity of a pure component when actual data have not been measured.

Viscosities of some of the more common gases have been measured at elevated pressures. Many charts and nomographs have been prepared which correlate the viscosity of gases as functions of temperature and pressure. More often, however, the engineer is concerned with determining the viscosity of gaseous mixtures at elevated pressures. The variation of the viscosity of gaseous mixtures with pressure has received little attention experimentally or theoretically. Boyd *(1)* measured the viscosity of hydrogen-nitrogen mixtures at elevated pressures. Clauson *(2)* has recently studied methane-nitrogen mixtures with a Rankine capillary at pressures up to 5000 p.s.i.a. These data plus the viscosity data on air at elevated pressures measured by Nasini and Pastonesi *(10)* and Kestin and Pilarczyk *(6)* represent all the data available on gaseous mixtures at elevated pressures.

This investigation was conducted for the Reactor Experimental Engineering Division of Oak Ridge National Laboratory. The pure components and mixtures investigated were of particular interest to the homogeneous reactor project.

The first phase of this investigation was the determination of the viscosity of helium and oxygen at elevated pressures over a temperature range of 200° to 450° C. The second phase was the determination of the viscosity of helium-oxygen, steam-helium, and steam-oxygen mixtures at elevated pressures and temperatures.

While no reliable method of predicting the viscosity of these mixtures from the pure component data is available, the data as presented should be of use to the practicing engineer. Possibly later the data on pure component and mixture viscosity will also be of value in testing the reliability of methods of predicting the viscosity of mixtures at elevated pressures.

APPARATUS

Description. The viscometer, shown in Figures 1, 2, and 3, consisted essentially of three parts, the gas feed and preheat section, the viscometer itself, and the gas bleed and flow measurement section.

Stainless steel pressure tubing, Type 304, 1/4 inch in outside diameter and 3/32 inch in inside diameter, was used throughout the apparatus with the exception of the capillary tube, and the capillary tube pressure taps. The feed and preheat section for permanent gases consisted merely of pressure tubing running from a supply tank either through a pressure regulator or directly into a coiled tube immersed in a salt bath. The regulator used was a diaphragm-type balanced pressure controller manufactured by the Victor Equipment Co. It was found to throttle gas pressures from tank pressure down to any lower pressure with no noticeable fluctuations in output pressure.

The preheater coil consisted of three sections of the pressure tubing 25 feet long coiled on 2-inch centers connected in parallel. Preliminary calculations showed that even under the laminar conditions maintained in the coil, the gas would be heated to virtually the bath temperature under the most extreme conditions of temperature encountered in this work. The preheater bath itself was a section of large pipe with a welded bottom. The cylinder thus formed was embedded in insulating cement and the entire apparatus was enclosed in a sheet metal shell. It was then filled with a eutectic mixture of potassium nitrate and sodium nitrite salts which was obtained from the American Cyanamid Corp. under the commercial name Aeroheat. Heat was supplied to the bath by three 1000-watt immersion heaters, connected in parallel through a variable transformer. Control was maintained by a Wheelco Potentiotrol to ±0.5° C. from the set point. Temperature in this and other

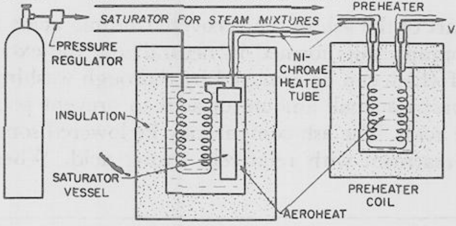

Figure 1. Feed and preheat sections of the viscometer

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