CHEMICAL COMPOSITION OF PROGRESSIVE PYRIDINE EXTRACTS FROM COAL

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SUMMARY

Progressive extraction of coal with pyridine for different periods of time has shown, by mass spectral and other analyses, that certain types of constituents are prominent in the early stages of extraction. Alkylbenzenes and phenols predominate in the first extract; polynuclear aromatics are found to be extracted later. The order of extraction is important in the mechanism of extraction of coals.

INTRODUCTION

Solvent extraction of coal has been used for many years in studying the constitution of coal. With pyridine, one of the best coal solvents, an appreciable fraction of the original can be extracted from high volatile and medium volatile bituminous coals. For these coals the extract is considered fairly representative of the whole coal, and experiments carried out on the extracts are therefore reasonably representative of the whole coal. The pyridine extract itself is generally considered to yield but little more information than does the parent coal; it is qualitatively quite similar to the coal.[1] But the extract does present a more tractable sample than the coal and makes possible further processing in solution. And, as shown before, there are quantitative differences between extract and residue.[1,2] The principal practice in solvent extraction is exhaustive extraction of the sample in order to obtain the highest yield possible. Dryden has looked closely at the effect of time of extraction on the yield of extract.[3]

In extracting coals under various conditions for mass spectrometric investigations, questions arose concerning a possible order of components coming out of the coal. Are all chemical entities extracted simultaneously? Are the following pairs extracted together or in succession: Aliphatics and aromatics, alkylbenzenes and alkylnaphthalenes, cyclic hydrocarbons and heterocyclics, acids and bases, etc.? Dormans and van Krevelen[4] found that molecular weights of the fractions increase with increasing extraction time; van Krevelen[5] has used such extraction data and polymer theory to find the interesting result that the extractability of coal solvents can be calculated.

To our knowledge no detailed characterization of the products from successive extractions, a method introduced by Rybicka,[6] has been carried out; the comparison of infrared spectra by Brown[1] is cited above. We have investigated possible effects of extraction time on composition of the extracts by utilizing progressive extraction, which differs from the successive extraction method of Rybicka[6] in that only one solvent is used and extraction times are varied from a few minutes to many hours. Mass spectrometry was used as the principal tool of investigation. Previously we have shown that low ionizing voltage mass spectra of coal extracts can determine quantitatively families of derivatives of various aromatic nuclei that are volatile at 300° C in a vacuum.[7] Preliminary experiments on the extraction process quickly showed that after many minutes of extraction there was no longer any difference, detectable by mass spectrometry, in the compositions of the extracts. It was concluded that the effects of progressive extraction would be illustrated best if samples were collected after 5 minutes, after 30 minutes, and after many hours of extraction.

EXPERIMENTAL PROCEDURE

The procedure for progressive extraction was: One gram of Pittsburgh coal of < 200 mesh was combined with 2 cc of pyridine. The mixture was shaken mechanically for 5 minutes, after which time the sample was opened and the solution immediately filtered to remove the extract and solvent from further contact with the coal. The extract solution was immediately centrifuged in order to remove the extract from any minute amounts of coal remaining. The coal thus separated from the extraction process was subjected to a further extraction with a new sample of added pyridine and the extraction was carried out for 30 minutes. At the end of 30 minutes the isolation of the extract was repeated as before. The process was then carried out again after 17 hours of extraction and an extract was again separated.

The mass spectrometer was a Consolidated Electrodynamics Corp. 21-103C with a heated inlet system fabricated in our laboratory and usually operated for this work at 290° C. Data on aromatics were obtained from low-ionizing voltage spectra.

The material analyzed by the mass spectrometer is that material that is sufficiently volatile to be observable. The remainder of each extract is unknown. The significance of the data obtained lies in the comparison of families of aromatics observed for the various extracts. Comparison of weight-average molecular weights with those published is not meaningful. It was determined that 90 percent of the material volatilized at 300° C from Pittsburgh coal is removed from coal by pyridine extraction. For this reason it is believed that the mass spectra of pyridine extracts are representative of the extract and of the coal. Good reproducibility of mass spectra of extracts has been established.[7]

RESULTS AND DISCUSSION OF RESULTS

Mass Spectra. The mass spectral analyses and the amounts of extract obtained in terms of percent of the original coal are indicated in table 1. Results of the mass spectral analyses indicate the following: (1) One- and 2-ring aromatics predominate in the 5-minute extract; higher aromatics predominate with longer extraction times. This is expected on the basis that lower molecular weight materials would be present in this extract.[4,5] (2) Percentages of benzenes, phenols, and naphthalenes were much greater for the 5-minute extract than for the other two extracts. (3) Yields of phenanthrenes-anthracenes and higher aromatics in the 5-minute extract are all less than those in the longer-time extracts. (4) The largest components found in the 5-minute extract are 4-ring, cata- and peri-condensed aromatics; the 30-minute and 17-hour extracts show components up through 6 rings peri-condensed. (5) The 30-minute extract contains slightly higher concentrations of 3-ring and smaller aromatics; the 17-hour extract contains slightly greater amounts of 4-ring and larger components. (6) Within a family of aromatics (e.g., C_6H_6, C_7H_8, C_8H_{10}, etc.) the distribution maximizes at the lowest molecular weight for the 5-minute extract. This is observed for benzenoids and phenols. Maxima for the other two extracts occur at higher molecular weights.

The larger concentration of phenols in the initial 5-minute extract is a significant finding. It is a direct indication that the basicity of pyridine is an important factor in coal extraction. Van Krevelen has shown that the differences in solubility parameters, δ, for coals and solvents are apparently of great importance in the extractability of coal solvents; he acknowledged that chemical properties are also likely to be very important.[5] Dryden[3] and Halleux and Tschamler[8] have shown that the availability of free electron pairs in hydrogen bonding solvents such as pyridine is important in interactions with acidic materials.

The beginning of the pyridine extraction process may be the "unlocking" of the coal structure through dissolution of phenolic structures, which are apparently hydrogen bonded (infrared spectra of coals indicate only hydrogen bonded OH, no free OH). However, it has not been established whether the "unlocking" process actually involves the breaking of hydrogen bonded structures.

Infrared Spectra. The spectra of extracts and residues were compared. As described by Brown, there are no qualitative differences, but there are semi-quantitative indications of changes in infrared absorption with extent of extraction.[1] Quantitative differences are appreciable as we found on comparing spectra of extracts and coals.[2] On the question of "unlocking" of hydrogen bonded structures in coal the infrared spectrum of the 5-minute extract indicates a slightly higher absorption at 1260 cm^{-1}. This absorption is attributable to phenolic structures, so a slightly greater concentration of phenolic structures is indicated for the initial, 5-minute extract. This result is at least some corroboration for the mass spectral indication of a higher phenol concentration in the 5-minute extract. The OH stretching band at 3300 cm^{-1} is not a reliable indication of phenolics in coal.

Aliphatic CH absorption in residues and extracts are compared in table 2. The residue from the 30-minute extract shows an absorbance decrease of 46 percent relative to the extract. Also it is interesting to note that the highest aliphatic C-H concentration occurs in the 30-minute extract; the aliphatic C-H content of the 5-minute extract is somewhat lower.

The CH content of the residues are all smaller than the corresponding extracts. Also, residues show decreasing C-H contents with increase in extraction, which is expected in view of the greater CH absorption bands found in the extracts.[1,2]

All absorption bands in the residues are slightly weaker and less well-defined than the corresponding bands in the extracts. The spectrum of a coal is most influenced by the sharper absorption spectra of the extract which are attributable to components high in hydrogen, both aromatic and saturated.

Aliphatic/Aromatic Ratios. Determination of the aliphatic/aromatic ratios of the various extracts were attempted by comparison of total ionization from mass spectra at low and high ionizing voltage. This comparison indicated that the 5-minute extract was slightly lower in aliphatic content. This result was considered dubious, but the infrared result apparently confirms it as the aliphatic CH content of the 5-minute extract is indeed slightly lower than that of the 30-minute extract (table 2).

Table 1.- Fractions from the progressive extraction of Pittsburgh seam (hvab) coal with pyridine[a]

Extraction time, hours	0.08	0.5	17
Extract, weight percent of coal	2.4	4.6	12.3
Aromatic compound types, including alkyl derivatives	Weight percent		
Mass spectral analyses:[b]			
Benzenes	29.2	1.9	1.9
Phenols	10.8	3.1	3.2
Dihydric and/or alkoxyphenols		.5	.5
Naphthalenes	25.4	13.5	12.2
Indenes; naphthols		1.1	.7
Indans		1.5	1.0
Indanols	1.8	2.2	2.1
Acenaphthenes	6.0	6.6	6.2
Acenaphthylenes; fluorenes	10.8	6.8	6.4
Anthracenes; phenanthrenes	3.0	10.6	9.9
Naphthalenes, phenyl substituted	5.5	7.8	7.6
4-ring, cata-condensed	2.5	7.9	8.6
4-ring, peri-condensed	4.5	11.2	11.9
3-ring, phenyl substituted	.5	7.2	7.9
5-ring, cata-condensed		8.0	8.9
5-ring, peri-condensed		7.0	7.6
6-ring, peri-condensed		3.1	3.4

a/ One of two complete runs.
b/ Compounds containing N, S, and non-phenolic O are probably also present.

Table 2.- Infrared spectra of coal extracts. Absorbance values at 2920 cm^{-1}, aliphatic C-H absorption band

Extraction time, hours	Absorbance at 2920 cm^{-1}	
	Extract	Residue
0.08	.22	.15
0.5	.26	.14
17.0	.16	.11

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