

ON THE STRUCTURE OF HUMIC ACIDS

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I. Introduction

About four years ago, the Research Council of Alberta initiated a series of coordinated, continuing studies from which several important inferences about the structure of humic acids can now be drawn. The present paper is intended briefly to review these studies and to outline those features of the humic acid molecule which can, in our view, be formulated with some confidence.

Almost all experimental data cited in the following sections were duplicated by working with humic acids derived from a weathered N. Dakota lignite*, and a weathered subbituminous coal occurring at Sheerness, Alberta. However, since these two materials displayed virtually indistinguishable behaviour, no attempt is here made to differentiate between the respective sets of results; and it is, in fact, tentatively contended that coal-derived humic acids may be regarded as chemical entities whose main structural features are essentially independent of their sources of origin.

II. The Molecular Weights of Humic Acids

In view of the then prevailing uncertainty about the size of the humic acid molecule, the initial study was concentrated upon renewed attempts to determine significant molecular weights (1). For convenience, a cryoscopic technique was used for this purpose, but in place of conventional solvents (e.g. acetamide, 2), sulfolane was employed. This solvent (3) offered several distinct and important advantages. It possesses an unusually high cryoscopic constant ($K = 65.5$ degrees - kg per mole); it affords a ready means for dissolving humic acids and completely drying the resultant solution; and it appears to eliminate disturbing effects due to solute association and/or dissociation. Generally ideal behaviour of sulfolane could, for example, be demonstrated by experiments with solutions containing such diverse compounds as benzoic acid, β -naphthalene sulfonic acid and biphenyl: in all instances, K proved to be quite independent of solute concentrations over the molality range 0.01 to 0.10. Direct evidence for the absence of association of solute molecules in a sulfolane solution could also be obtained from infrared data - notably from analysis of the -COOH and -OH stretching frequencies of simple analog compounds.

* Commercially marketed as Baroid Carbonox.

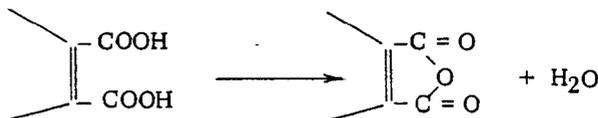
Using the sulfolane method with a series of carefully fractionated humic acids, molecular weights ranging to ca. 10,000 were recorded (1) and broadly confirmed by sedimentation velocity measurements.

It is of some interest to note that while molecular weights of the order of thousands stand in marked contrast to previously reported cryoscopic data, they are in general agreement with semi-quantitative diffusion measurements reported, inter alia, by Dryden (4).

III. The Disposition of Peripheral Functional Groups

Estimates of the concentrations of functional groups by established methods (5, 6) yielded results comparable to those reported for humic acids by other laboratories. Typical values (7) were: $-\text{OCH}_3$ 1.7, phenolic $-\text{OH}$ 2.7, and $-\text{COOH}$ 4.3 milliequivalents per gram. More detailed studies, however, permitted some refinement of these data and, more important, inferences about the disposition of certain functional groups around the molecular periphery.

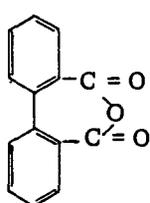
When solutions of humic acid in sulfolane were heated to $170^\circ - 200^\circ\text{C}$ under reduced pressure and subsequently examined by infrared spectroscopy, the intensity of the original carboxyl carbonyl absorption at 1735 cm^{-1} was found to be greatly reduced, and two new bands centring at 1850 and 1785 cm^{-1} were observed (Figure 1). Since identical absorptions were seen in the infrared spectra of phthalic and 1,2-naphthalic anhydrides formed in hot sulfolane, these bands were assigned to 5-membered ring anhydrides of humic acid, i.e. to simple dehydration products of the type,



and it was concluded that a substantial number of $-\text{COOH}$ groups in the humic acid molecule occupy mutually adjacent sites. Six- or 7-membered ring anhydrides could be ruled out because of their infrared absorption at quite different frequencies, and still larger cyclic anhydrides were discounted by the rather narrow band separation generally seen in the spectra of such compounds.

When, on the other hand, humic acid is refluxed with acetic anhydride, a more complex situation is created. The intensity of the original $-\text{COOH}$ band is again greatly reduced, but now at least four new bands (at 1850 , 1820 , 1785 and 1745 cm^{-1}) are found; and the 1785 cm^{-1} band is, compared with the 1850 cm^{-1} absorption in the same spectrum, substantially more intense than in the spectrum of humic anhydride formed in hot sulfolane (Figure 1).

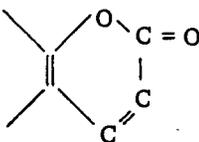
On the assumption that reaction with acetic anhydride forms, among other products, the same anhydrides as are produced by heating sulfolane solutions of humic acid, cyclic 5-membered ring anhydrides were therefore now supposed to account for only a part of the 1785 cm^{-1} absorption, and a number of theoretically possible contributing structures were examined. Among these were cyclic anhydrides of type (I), open chain anhydrides, including mixed anhydrides (II), lactones (III), esters (presumably of the phenolic acetate type IV), and esters and/or anhydrides formed between molecules of humic acid.



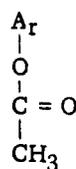
I



II



III



IV

The results, partly based upon extended experimentation with exhaustively methylated, alkali-hydrolyzed humic acid and acetyl analyses (8) led to the following conclusions(7):

- (a) Approximately 80% of all $-\text{COOH}$ groups existing in humic acid occupy sites permitting the formation of cyclic ring anhydrides.
- (b) Approximately one-fifth of all $-\text{COOH}$ groups form linear mixed anhydrides when humic acid is reacted with acetic anhydride (but not in sulfolane) and must therefore exist as isolated groups or in odd-numbered groups on adjacent ring sites.
- (c) Of the several, theoretically possible 6- and 7-membered ring anhydrides, only anhydrides of the diphenic type (I) are consistent with experimental evidence.

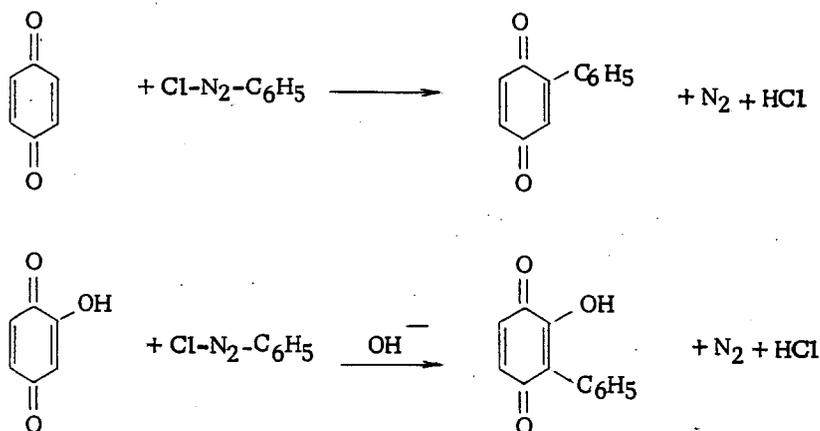
Since a part of the strong 1785 cm^{-1} band in the spectra of humic anhydrides formed by reaction with acetic anhydride can also be ascribed to esters -- and in particular to esters of polyfunctional phenols -- it is tentatively further thought possible that a proportion of the total $-\text{OH}$ content of humic acid may occur as groups of 2 or 3 $-\text{OH}$ residues on the same ring or condensed aromatic nucleus. This view is, however, subject to rather severe limitations since $-\text{OH}$ residues located ortho or para to each other would undoubtedly be converted to quinones by the conditions under which humic acids form.

IV. Quinone Structures

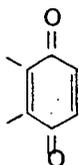
When humic acid is reacted with diazotized sulfanilic acid, a water-soluble derivative forms through introduction of $-N=N-C_6H_4-SO_3H$ and/or $-C_6H_4-SO_3H$. Both mechanisms, i.e. interaction with phenolic structures or with quinones, are consistent with infrared spectral evidence in that both would lead to the new absorptions indicative of the presence of sulfonic groups which are observed (Figure 2b); but since the former requires introduction into the humic acid molecule of two nitrogen atoms per additional sulfur atom (which analysis shows not to occur to any significant extent), it has been concluded that the dominant reaction involves a free radical attack on quinones at an available position.

Proceeding from this recognition, an interesting route to further elucidation of the structure of humic acid can be developed (9).

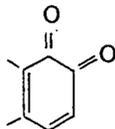
Of the two most probable theoretical free radical mechanisms by which a $-C_6H_4-SO_3H$ group is introduced into the humic acid molecule, one — a Gomberg reaction — must be ruled out on evidence offered by Gomberg and Pernert (10), Grieve and Hey (11), and Walling (12). There remain therefore only interactions of the type



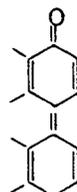
from which it follows that humic acid molecules reacting with the diazonium salt must contain one or more of the basic structures V, VI and VII.



V



VI



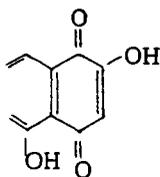
VII

Now, the possible existence of these (or similar) entities in humic acid has been recognized for some years. But more unequivocal information about them has now been obtained by infrared studies on methylated* and subsequently acetylated humic acids. Of particular importance was the existence in the spectra of these compounds of a fairly intense absorption band at 1660 cm^{-1} (Figure 2d), i.e. at the same frequency at which a wide range of relatively simple quinones (cf. Table I) show a diagnostic absorption. If this observation is viewed against the background of polarographic evidence (13) and x-ray diffraction data (14) — which preclude polycondensed ring systems of more than 4-5 rings in low and medium rank coals — it can be concluded with reasonable safety that while simple benzoquinones cannot be postulated, possible structures could include OH-substituted naphthoquinones and anthraquinones as well as more complex systems containing heterocyclic oxygen. Detailed examination of the infrared spectra obtained in these laboratories leads, in short, to the conclusion that structures VIII and IX appear to be the simplest consistent with presently available evidence.

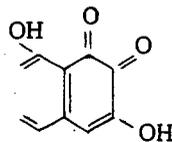
Table I. Carbonyl stretching frequencies of quinones

Compound	Frequencies cm^{-1}	Phase
1,4-Benzoquinone	1665	Mull
1,2-Benzoquinone	1669	CCl_4
1,4-Naphthoquinone	1662	Mull
1,2-Naphthoquinone	1678	CCl_4
Anthraquinone	1671	Mull
9,10-Phenanthraquinone	1670	Mull
Anthrone	1654	Mull
Bianthrone	1657	Mull
Bianthranyl	1656	Mull
Anthanthrone	1650	Mull
Dibenzypyrenequinone	1645	Mull
3,8-Pyrenequinone	1636	Mull
3,10-Pyrenequinone	1640	Mull
Dibenzanthrone	1645	Mull
isoViolanthrone	1646	Mull
Pyranthrone	1642	Mull
Helianthrone	1642	Mull
1,2-Chrysenequinone	1661	Mull
1,2-Benzanthra-9,10-quinone	1664	Mull
1,2,3,4-Dibenzanthraquinone	1662, 1749	Mull
1,2,5,6-Dibenzanthraquinone	1652	Mull
3,10-Perylenequinone	1650	Mull

- * Initial methylation was designed to block all readily accessible hydroxy groups of phenols and carboxyls and thereby to avoid interference due to acetate esters and anhydrides in the 1800 and 1740 cm^{-1} regions of the infrared spectra.



VIII



IX

It is, in this connection, noteworthy that estimates of the concentration of quinones in humic acid (9) by several different techniques yielded values of the order of 0.8 ± 0.2 milliequivalents/gm. The corresponding concentration of hydrogen-bonded quinones, which was derived from acetyl determinations on the assumption that each quinonoid oxygen is H-bonded to one phenolic -OH that can in turn be acetylated by acetic anhydride, was found to be 0.63 milliequivalent/gm. (and thus in good agreement with previously reported values; 15, 16, 17, 18).

An estimate of the carboxyl carbonyl:quinone ratio was obtained from the relative intensities of the 1660 and 1735 cm^{-1} absorptions on the assumption that the relationship between these bands was similar to that prevailing in the infrared spectrum of 2-(p-carboxyphenyl)-1, 4-naphthoquinone (which was chosen as a suitable model compound - Figure 2e). This ratio was found to be 14 as compared with 6 calculated from analytical data. While this discrepancy is large, it is, in view of the obvious inaccuracies entailed in the estimation via infrared spectra, not excessive.

With respect to the water-solubility induced in the humic acid derivative by reaction with the diazonium salt it might also usefully be noted that this appears only partly to arise from the introduction of sulfonic acid residues; a contributory factor seems to be cleavage of $-\text{CH}_2-$ bridges and the consequent reduction in molecular size. In support of this view attention is drawn to the identification of formaldehyde among the reaction products. The formative step for this would be



Recent experiments in these laboratories have shown that coals can undergo similar reaction with diazotized sulfanilic acid, but that the yield of water-soluble products decreases rapidly with increasing rank. While a lignite (C = 71% d.a.f.) showed after two treatments a ca. 80-90 per cent conversion, two subbituminous coals (C = 74 and 80% resp.) yielded after several treatments only about 50 to 70 per cent water-soluble derivatives, and a bituminous coal (C = 87%) proved almost wholly unreacted.

An alternative technique now actively being explored, i.e. sulfo-methylation (19,20,21) by means of $\text{CH}_2=\text{O}$ and NaHSO_3 leading to the addition of $-\text{CH}_2\text{SO}_3\text{H}$ to the aromatic nuclei, has been shown to produce analogous results (and, if anything, to be even more strongly affected by coal rank). It is, however, considered that yields of water-soluble products obtainable by this reaction, or by reaction with a diazonium salt, can be significantly increased by mild preliminary oxidation of the coal.

V. The Skeletal Structure

From measurements of the viscosities of humic acid solutions it has been concluded that humic acids may resemble flexible, linear polyelectrolytes (22). This conclusion, however, is considered untenable since humic acids show surprising stability in high-intensity ultrasonic fields (23); even prolonged exposure at frequencies up to 2 mc/s and intensities up to ~ 10 watts/cm² have failed to induce molecular rupture. Since the molecular weights of the test samples exceeded 5,000, i.e. a size at which linear molecules would degrade, it has, in the light of x-ray diffraction evidence, been postulated that the most probable skeletal structure involves relatively small (3-4 condensed ring) aromatic systems interlinked by mixed $-\text{O}-$ and $-\text{CH}_2-$ bridge structures. Linkage by $-\text{O}-$ only was ruled out by the fact that pyrolysis of humic acids yields considerable quantities of tarry matter (and, subsequently, by the detection of $\text{CH}_2=\text{O}$ as a by-product of reaction with diazonium salts, cf. above).

To test this general concept in detail, and to develop means for quantitative estimation of $-\text{CH}_2-$ and $-\text{O}-$ concentrations, current studies in these laboratories are directing attention to reactions of humic acid with (a) BF_3 in phenol, and (b) Na in liquid ammonia.

Interactions between coal and BF_3 -phenol have recently been reported by Heredy and Neuworth (24) who found 60-80% conversion of a high volatile bituminous coal into soluble products, presumably by the rupture of methylene bridges between aromatic nuclei. We have now observed humic acids to be completely soluble in this reagent mixture. The reaction appears to be accompanied by considerable molecular degradation* and several direct comparisons are possible between Heredy and Neuworth's and our results. Thus:

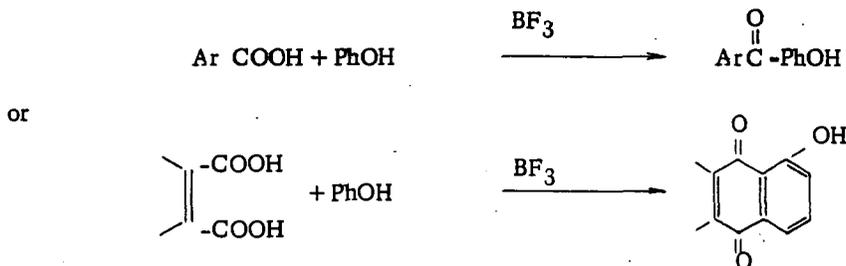
(a) A considerable increase in weight results from interaction between humic acid and BF_3 -phenol (e.g. from 13.6 to 29.0 gm); this indicates a combined phenol content of 53.2% which compares with a value of 55.7% reported by Heredy and Neuworth for one of their fractions.

(b) The reacted, BF_3 -phenol-soluble humic acid is, like the soluble coal fraction (above) of Heredy and Neuworth, soluble in methanol.

* Quite low molecular weight crystalline reaction products have been isolated from the mixture and tentatively identified by us. Details will be published elsewhere in due course.

(c) The phenolic -OH concentration in reacted humic acid amounts to ca. 5.1 milliequivalents/gm (as compared with 4.3 milliequivalents/gm for the reacted coal fraction referred to in (a) above).

A particularly noteworthy observation is that the carboxyl groups initially present in humic acid are completely eliminated by reaction with BF_3 -phenol — probably as a result of BF_3 -catalyzed condensation of the type (26):



If a scheme of this form is tentatively accepted, the further assumption that each $-\text{CH}_2-$ group reacts with two molecules of phenol leads to the conclusion that methylene bridges occur in humic acid at the rate of one per every ~ 200 molecular weight units. An assumption that each $-\text{CH}_2-$ reacts with a single phenol molecule (24) would halve this estimate. If it is (quite reasonably) supposed that a proportion of $-\text{CH}_2-$ will survive the oxidation processes by which coal is converted into humic acid, even the first estimate is in good agreement with a value of ca. one $-\text{CH}_2-$ per every 100 molecular weight units in coal (26).

The interest attaching to reactions with sodium in liquid ammonia arises primarily from the ability of this reagent mixture to cleave aromatic ether linkages which are, for various reasons, presumed to exist in humic acid (and coal). Detailed studies of this aspect in our laboratories are still in their initial stages; but it is worth noting that while reaction between humic acid and Na-NH_3 leaves a substantial residue of insoluble material, the derivative obtained from reaction with BF_3 -phenol becomes completely soluble in acetone. We are tentatively inclined to the view that this differentiation lends some support to the existence of mixed $-\text{CH}_2-$ and $-\text{O}-$ bridges in the parent molecule.

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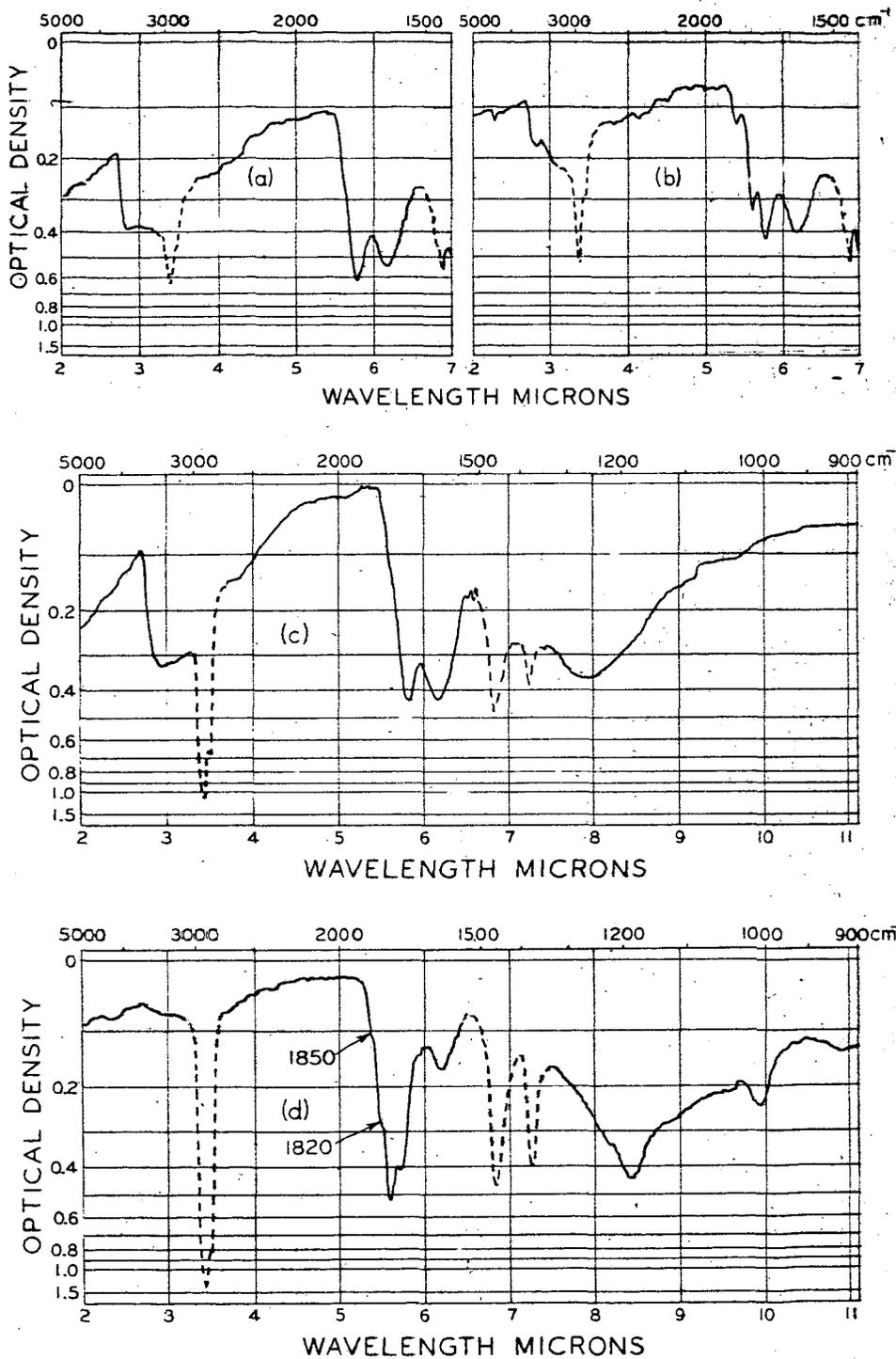


FIGURE 1. Humic acids and derivatives

- (a) parent humic acids (sulfolane mull). (c) parent humic acid (Nujol mull).
 (b) humic acids heated in sulfolane (sulfolane mull). (d) humic acids treated with boiling acetic anhydride (Nujol mull).

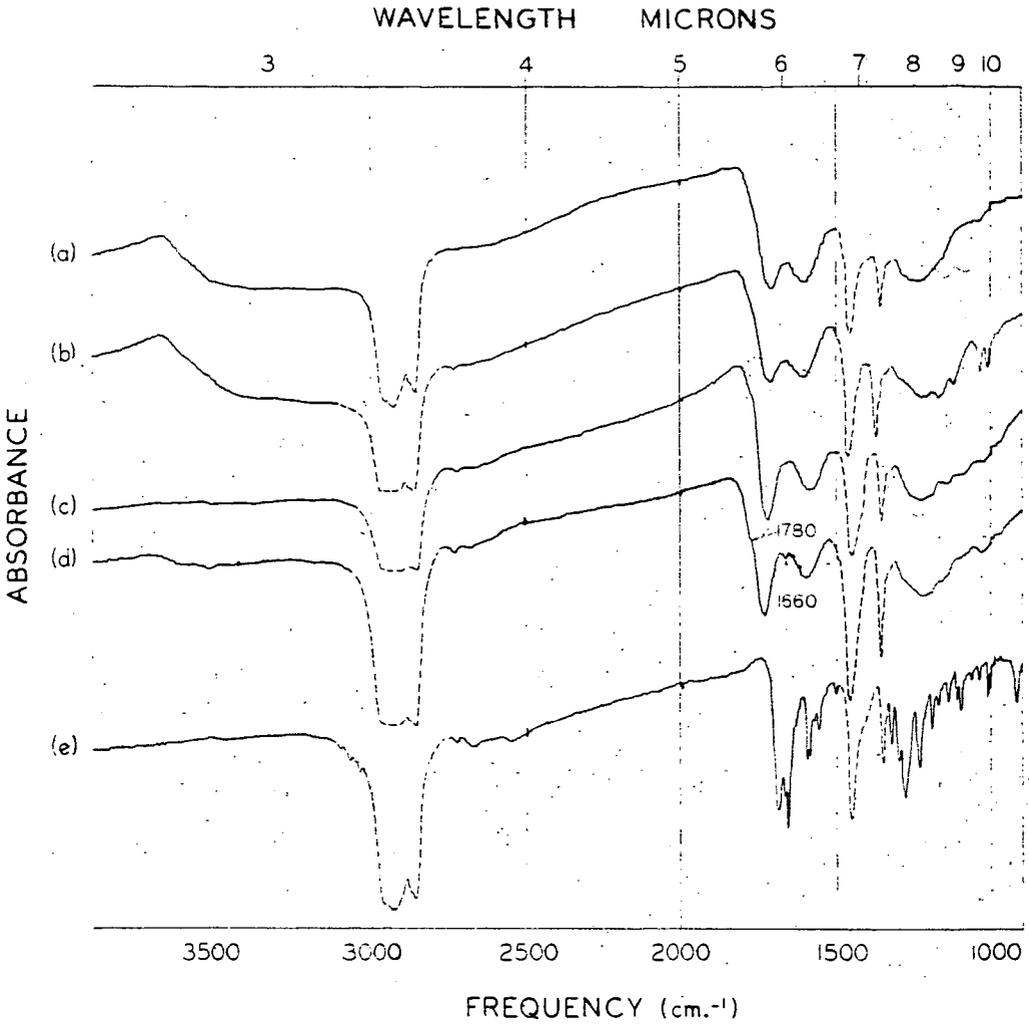


FIGURE 2. Humic acids and derivatives.

- (a) parent humic acids.
- (b) treated with diazotized sulfanilic acid.
- (c) methylated.
- (d) product of (c) treated with acetic anhydride.
- (e) 2-(p-carboxylphenyl)-1,4-naphthoquinone.

HUMIC ACIDS FROM LEONARDITE -- A SOIL CONDITIONER
AND ORGANIC FERTILIZER

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The term "humic acid" was first applied in 1826 by Sprengel (9) to that brown amorphous precipitate which is obtained by acidifying the alkali extract of decayed organic matter in soil. Since the inception of the term, humic acids have been extracted not only from soil but also from peat, brown coal, oxidized bituminous coal, and even from artificial materials obtained in the laboratory by action of inorganic acids or oxidizing agents on carbohydrates, proteins, and phenols. Odin (8) in 1922 redefined humic acids as yellow-brown to black-brown substances of unknown constitution, formed in nature by decomposition of organic materials under atmospheric influence or in the laboratory by chemical action. Humic acids can split off hydrogen ions and form typical salts with strong bases and usually are insoluble in water, soluble in alkali, and reprecipitated by acid. In general, humic acids are not chemically uniform substances, but are hydrophilic, reversible colloids with molecular weights varying from 300 to as high as 10,000 units. Their micelles carry a negative charge. The alkali solubility of humic acid is due to carboxyl and phenolic hydroxyl groups which account for about 22 percent of the weight of the molecule.

Humic acid is an essential part of soil. It is this material, present in good soil, that fixes nitrogen, makes available to the plant, through base exchange, the soil nutrients, and improves the physical structure of the soil. In recent years, much research has been conducted, particularly in India, Japan, Germany, Russia, and France, on replenishing the depleted humic acids of soils with the so-called "regenerated humic acids" obtained by oxidation of coal. These regenerated acids, which closely resemble the natural humic acids, have either been added directly to the soil or first supplemented with plant nutrients. Greenhouse and field tests have shown that these humic acid preparations improve plant yields (3), decrease loss of moisture from the soil (6), and increase the workability of the soil (2).

As a convenient and commercial source of humic acids, extensive reserves of naturally-oxidized lignite occur with virtually all lignite outcrops in North Dakota. This naturally-oxidized material, which contains up to 86 percent humic acids on a moisture-and-ash-free basis, has been given the name "leonardite," after A. G. Leonard, first director of the North Dakota Geological Survey, who did much of the early studies on these deposits (1). Leonardite is a coallike substance similar in structure to lignite, but significantly different in its oxygen and ash contents. In Table 1 the ultimate analyses of lignite, leonardite, lignite oxidized with air in the laboratory at 150° C, and humic acid extracted from leonardite with 1N NaOH are compared. The ash content of leonardite varies from mine to mine but is usually between 15 and 30 percent on a moisture-free basis.

TABLE 1. - Analyses of lignitic materials, percent

	Leonardite	Lignite	Oxidized lignite	Humic acid extracted from leonardite by 1N NaOH
Ash (mf)	18.7	10.0	10.7	3.9
Hydrogen (maf)	4.0	5.1	2.9	3.4
Carbon (maf)	65.2	72.8	65.4	63.5
Nitrogen (maf)	1.3	1.2	1.4	1.3
Oxygen (maf)	26.6	19.9	29.2	31.1
Sulfur (maf)	2.9	1.0	1.1	0.7

AMMONIATION OF LEONARDITE

Nitrogen-enriched coal humic fertilizers have received much emphasis in the past few years. Recent investigations have indicated that these products perform well as conventional fertilizers and release nitrogen more slowly. The main problem in technology is to develop a product with sufficiently-high nitrogen content (around 20 pct) which will still remain commercially competitive.

To determine if leonardite could be ammoniated to a product containing sufficient nitrogen for use as an organic fertilizer, samples were prepared by three different methods: (1) Ammoniation in an aqueous slurry, (2) ammoniation in an upward moving gas stream through a column of dried leonardite, and (3) ammoniation under pressure of 2,000 psig at 200° C. The nitrogen analyses of these variously ammoniated leonardite samples and the analysis of an aqueously ammoniated humic acid extracted from leonardite appear in table 2. The increase of nitrogen content of leonardite, even under radical conditions, is not sufficient for it to be used as an organic fertilizer. The nitrogen content of the ammoniated humic acid increased 2.5 times over that of the correspondingly ammoniated leonardite sample. The higher ash content, as well as the 15-percent nonhumic carbonaceous material in the leonardite, accounts for the decreased reactivity with ammonia. Therefore, to prepare a high-nitrogen organic fertilizer, the humic acids would first have to be extracted from the leonardite.

TABLE 2. - Nitrogen analyses of variously ammoniated samples, percent
(Moisture-free basis)

Sample	Method of ammoniation		
	1	2	3
Leonardite	3.87	2.82	11.15
Humic acid	8.13	-	-

RECOVERY OF HUMIC ACIDS FROM LEONARDITE

One part of the work at this laboratory was to find an inexpensive, rapid method for obtaining from leonardite bulk quantities of low-ash humic acids which could be used in preparing a soil conditioner and high-nitrogen-content organic fertilizer. The humic acids in leonardite are bound to the ash largely as insoluble calcium salts. Therefore, to recover the humic acids requires not only a physical means

of removing the clay and sand, but also a chemical treatment to displace the calcium ion. In the past, alkali extraction of the humic acids with removal of the insolubles by centrifuging the humate solution was the standard procedure for obtaining low-ash humic acids (5). The alkali extraction process, however, requires not only fresh alkali for each lot of humic acid prepared but also an equivalent amount of acid to set the humic acid free, both of which are used up in the process. The large volumes of water, which must be used to obtain a low-ash product, plus the unfilterable nature of the alkali humate solution and acid-precipitated humic acid, make the alkali extraction of humic acids unattractive. The problem of eliminating alkali extraction as the method of preparing low-ash humic acids was approached by two different routes: (1) Removing the ash physically and chemically from the leonardite, leaving a carbonaceous product containing around 85 percent humic acid, and (2) extracting the humic acid from the leonardite with an organic solvent that could be reclaimed for further extractions.

Float-Sink Process. Figure 1 schematically represents the process that was used in our experiments. Partially-dried, pulverized leonardite was added to a separatory funnel containing CCl_4 as the dense medium. The float fraction containing the humic acids was transferred to a filter, and the CCl_4 was removed. The product was washed first with a dilute H_2SO_4 solution, then with warm water. The results of this experiment appear in table 3. A ZnCl_2 solution was tried in place of CCl_4 , but absorption of the solution on the carbonaceous material caused the latter to sink, resulting in a low yield of humic material.

TABLE 3. - An examination of the float-sink process, moisture-free basis, results given in percent

<u>Feed</u> <u>Ash</u>	<u>Product</u>			<u>Tailings</u>	
	<u>Yield</u>	<u>Ash</u>	<u>Humic Acid</u>	<u>Yield</u>	<u>Ash</u>
17.7	73.1	3.5	89.0	17.4	56.8

Note - Not included in data is loss of water-soluble material.

Flotation Process. The flotation process for ash separation is schematically depicted in figure 2. The as-received, pulverized leonardite was added to the flotation cell, which contained a lignite-tar creosote fraction as a frothing agent. The froth was collected on a filter, and the filter cake was washed with dilute H_2SO_4 , followed by warm water. Results of a typical experiment in this process appear in table 4.

TABLE 4. - Analysis of the flotation process, percent

<u>Feed</u>		<u>Product</u>		
<u>Moisture</u>	<u>Ash (mf)</u>	<u>Moisture</u>	<u>Ash (mf)</u>	<u>Yield (mf)</u>
9.5	18.2	6.0	11.3	13.6

Organic-Solvent Extraction Process. The use of an organic solvent for extraction of humic acids would be most attractive if the solvent could be reclaimed by distillation and reused without reaction with or being absorbed on the humic acids. Polansky and Kinney (7) made an extensive survey of organic solvents and solvent mixtures regarding their ability to disperse humic acids from nitric acid-oxidized bituminous coal. They concluded that the most economical and most easily handled solvent for the commercial extraction of humic acids is a mixture of

acetone and water. Fowkes and Frost (4) showed that an acetone-water solution would extract humic acids from leonardite provided the leonardite was pretreated with dilute mineral acid. The amount of humic acids extractable was directly proportional to the amount of mineral acid used in the pretreatment. The several preliminary experiments conducted revealed that the most efficient extraction was accomplished using one liter of 80-20 acetone-water (percent by volume) and 10 grams of HCl (basis: hydrogen chloride) per 100 grams of leonardite (moisture-free). Ten grams of HCl per 100 grams of leonardite is slightly in excess of the acid that will be necessary to replace the calcium ion with hydrogen ions in an average leonardite sample. Sulfuric acid was tried in place of HCl as the source for the displacing H-ions, but the resulting CaSO_4 , mixed with the humic acids, resulted in an unfilterable product with a high ash content. In the first experiments, the mode of extraction was a countercurrent column. An acetone-water-HCl pretreated leonardite slurry was added to the top of the column while a solution of acetone-water was forced slowly upward through the slurry. The yields of humic acids were good, but the ash content of the product was high, indicating some carryover of ash. Later experiments showed that sedimentation of ash and nonhumic carbonaceous material in an acetone-water-HCl solution is quite rapid; thus a simple settling tank replaced the countercurrent column in the process. A flow diagram of the process appears in figure 3. The results of the experiments appear in table 5.

TABLE 5. - Analysis of the acetone-water-HCl extraction of humic acid from leonardite, moisture-free basis, percent

Feed Ash (mf)	Product			Tailings	
	Yield (mf)	ash (mf)	NaOH-soluble (mf)	Yield (mf)	Ash (mf)
17.8	64.9	1.8	96.8	31.1	38.2
			{ C 63.5		
			{ H 3.8		
	Elemental		{ N 1.0		
	(maf)		{ S 0.7		
			{ O 31.0		

Note - Not included in data is loss of water- and acid-soluble material

DISCUSSION

A comparison of the three processes investigated reveals the drawbacks of the float-sink and the flotation processes. The float-sink separation requires a non-polar medium, carbon tetrachloride, which is absorbed to some extent on the leonardite. The use of CCl_4 , plus the fact that the leonardite must be partially dried before separation, makes this process unattractive commercially. The flotation process did not produce the desired results. Owing to the low hydrophobicity of leonardite, caused by the large number of carboxyl and hydroxyl groups on the micelle's periphery, the yields of humic acids were low and their ash contents high. Attempts to precondition the leonardite with a light neutral fraction of coal tar to increase its hydrophobicity failed. Changing the frothing agents several times also gave poor results. The acetone-water-HCl extraction of humic acids lends itself most favorably to a commercial process. The yield of low-ash product is high. The acetone is easily recovered by distillation at a low temperature, and the loss is very small. Acetone does not react with, nor is it absorbed on, the humic acids. The process requires

simple equipment (a sedimentation setup works quite well), and the insolubles settle rapidly. The humic acids are easily filtered once the acetone is removed, and a minimum amount of wash water is needed to obtain a low-ash product.

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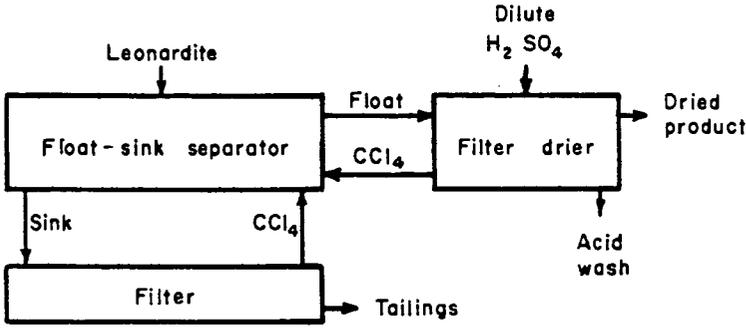


Fig. 1 Float-sink separation.

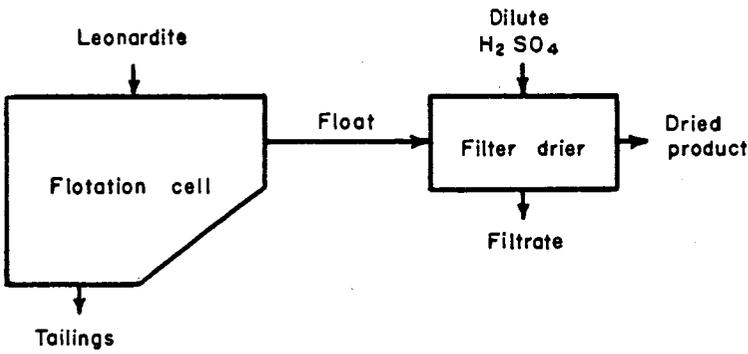


Fig. 2 Flotation process.

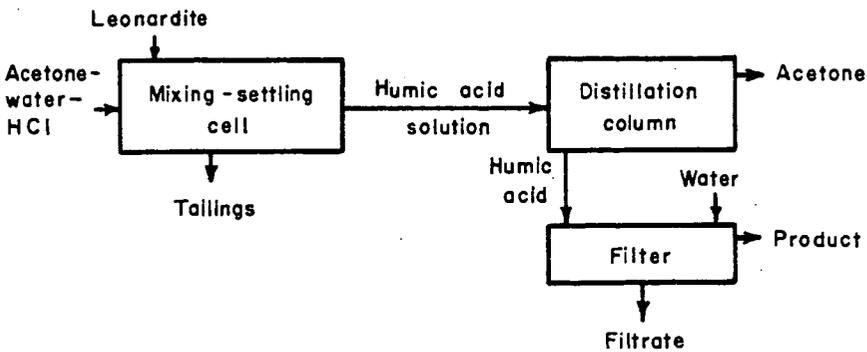


Fig. 3 Organic-solvent extraction.

HUMIC ACIDS FROM SUBBITUMINOUS COAL -
A STUDY OF CONTROLLED DRY OXIDATION

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During the past few years, advances in humic acid chemistry have made it increasingly clear that humic acids offer an interesting and fairly direct route to large-scale chemical utilization of coal, and several commercial products containing (or derived from) them are, in fact, already being marketed (1,2,3). Despite this progress, however, processes by which humic acids form from and in coal are, like their detailed structure, still only incompletely understood and merit further investigation.

By definition, humic acids are brownish-black, alkali-soluble solids which can either be recovered from naturally weathered coals (4,5) or, alternatively, be prepared by controlled oxidation. The latter procedure, which is in principle to be preferred to reliance on necessarily random and somewhat uncertain natural processes, may take two basic forms. Pulverized coal can either be heated and reacted with air or oxygen (or with an oxygen-enriched air stream), in fluidized or static bed (6,7,8,9,10); or the coal may be suspended, conventionally, in hot aqueous alkali and treated under pressure (11,12,13) with air or oxygen. The choice between these techniques appears, at this time, to be largely a matter of personal preference since each has distinct advantages and disadvantages. For example, while wet oxidation will generally entail a substantially shorter reaction period than the dry process, its greater severity will usually mean lower yields of humic acids (and a proportionately greater concentration of low molecular weight, water soluble, degradation products in the final product mixture)(11).

Regarding the formation of secondary degradation products as basically undesirable, the Research Council of Alberta concentrated an initial study of the mechanism of the coal \rightarrow humic acid conversion on dry oxidation. This paper reports the behaviour of a typical Alberta subbituminous coal in such a process.

Experimental Procedure

In order to permit meaningful measurements which could be related to the ambient conditions under which oxidation was carried out, an apparatus of the form illustrated in Figures 1 and 2 was used. This afforded a gas-tight, closed circuit with provisions for pressure regulation, gas sampling and withdrawal of coal aliquots without interruption of the conversion process. As indicated in the diagrams, the total volume of the apparatus was approximately 2,200 cc.

Oxidation of the coal was achieved by means of dry oxygen which was introduced into the apparatus at the same rate at which it was consumed and which was thus maintained at a constant pre-selected pressure throughout each experiment. By arranging one-half of the constant-head oxygen supply bottle as a calibrated cylinder, accurate measurements of O₂-consumption rates were possible. The total pressure was maintained at 1 atmosphere.

Instantaneous oxygen concentrations within the apparatus were continuously recorded on a Beckman F3 oxygen analyzer.

At the commencement of a run, the oxygen bottle was filled and the measuring cylinder completely topped with water. 15.00 gm of coal (-65 + 150 mesh Tyler), vacuum dried at 50°C were then charged into the fluidizer, the CO₂ and H₂O absorbers weighed (to the nearest 0.01 gm) and the fluidizer brought to the selected reaction temperature.

During the first 30 minutes after attainment of the reaction temperature, the rate of oxygen consumption would occasionally exceed the capacity of the supply valve, and in such cases, oxygen was furnished from a secondary source. By this means, it was possible to maintain the oxygen content uniform within $\pm 1\%$.

As the run progressed, 1 cc gas samples were withdrawn from time to time and submitted to gas-chromatographic determination of oxygen (as a check on the performance of the Beckman analyzer), nitrogen (as a test for leaks) and carbon monoxide. At regular intervals, 0.1 - 0.2 gm coal samples were also withdrawn for infrared spectroscopy, elemental analysis and functional group determination.

Measurements of alkali-solubles in these coal samples — conventionally accepted as a measure of humic acid content — were made by Kreulen's method and expressed as percentage humic acids in the sample (14). A minor modification in Kreulen's method was however, introduced in order to secure greater precision. Since the results obtained are distinctly time-dependent (cf. Figure 3) — presumably because of further oxidation in aqueous alkali — and since this drift could not be eliminated by blanketing with N₂, humic acid contents were determined at 2 and 24 hours after initial suspension in alkali and extrapolated to zero time. Since the titre increased linearly with time for at least the first 30 hours after extraction, this procedure was considered justified and relatively error-free.

Results

Experiments so far have been limited to a single subbituminous coal with C \sim 71%, H \sim 4.2%. Results obtained are exemplified by Figure 4 which reproduces data gathered during a single experiment in which the oxygen concentration and temperature were held constant at 22.5% and 250°C, respectively. It will be observed that the carbon and hydrogen contents of the solid move asymptotically towards limiting values, while carboxylic acid concentration and total acidity (total acidity = carboxyl + phenolic OH) pass through a definite, broad maximum. The humic acid concentration likewise passes through a maximum. CO (not shown in Figure 4) appeared in the early stages of conversion, reached a maximum at 10 hours (5-15% by volume of gas) and disappeared completely beyond 65 hours. The significance of this observation is at this time unknown.

Material balances, which were established in all runs, checked within 5%. Experimental conditions could be duplicated to within \pm 1% in oxygen concentration and \pm 2°C in temperature, and the various measured quantities as shown in Figure 4 agreed to within \pm 5%.

Figure 5 represents a repeat of the experiment illustrated in Figure 4, but this time extended to 450 hours. No measurements were made before 150 hours had lapsed. Beyond the first 150 hours, only insignificant changes appear to take place in the composition of the solid, but as shown by the continuous oxygen consumption, there is a steady loss of coal and already formed humic acid to carbon dioxide and water. At the conclusion of the test, only 46% of the original charge was recovered as compared with 66% in the test stopped at 150 hours.

Similar experiments were carried out at temperatures between 150 and 300°C, and at oxygen concentrations between 10 and 100%. Figure 6 illustrates the relation between temperature and functional groups at constant oxygen concentration. The same relationship was found in tests where the oxygen concentration was varied.

A summary of 20 experiments so far concluded in the study here under review is contained in Figure 7 a and b. For the particular coal examined in these runs, the pattern shows optimum humic acid conversion and recovery after 65 hours at 250°C and 25% oxygen concentration.

The humic acid content in the oxidized coal ran to ca. 95% and some 75% total solids (based on the initial charge) were recovered. The total (phenolic -OH plus -COOH) functional group concentration in the humic acid formed under these conditions runs to 10 milliequivalents/gm. The limiting C-H values are 61% and 1.8% respectively.

Discussion

Whether another coal would significantly alter the general pattern of results shown in Figure 7a and b, or whether it would only change the position of the maxima remains to be determined. Nor can anything, at this time, be said about possible catalytic effects of coal ash on the conversion process. Despite these limitations, however, the data so far at hand provide worthwhile new information.

As might be expected, variations in oxygen concentration and temperature tended to work in the same direction. Below 10% oxygen or 150° C, no significant reaction was observed. Above 80% oxygen or 300° C, rapid and complete oxidation of the coal to CO₂ and H₂O was found. For any conditions within this general range the carboxylic acid content rose through a maximum and then decreased (although the measurements were not always continued into the fall-off region). The total acidity likewise passed through a broad, but less pronounced maximum. These maxima occurred at shorter times as oxygen concentrations or temperatures increased.

The results illustrated in Figure 6 show that a temperature variation markedly influences the carboxyl concentration, which may range from 1 - 9 m.eq./gm. On the other hand, the total acidity is much less temperature dependent. Production of a humic acid principally characterized by either -OH or -COOH contents is, accordingly, dependent upon a more careful choice of experimental conditions than would be required if a predetermined total acidity only is to be afforded.

Since other results — though as yet incomplete — indicate that oxygen concentration has the same effect as temperature on the content and composition of the functional groups, the same statement may apply to this variable.

Another finding relates to the infrared spectra of partially reacted coal samples. These spectra, which were measured in order to gain information about reaction products not encompassed by other methods employed, did in some (but not all) series show pronounced absorption bands at 1850 and 1785 cm⁻¹ and thereby indicate the existence of 5-membered ring cyclic anhydrides (15, 16). To our knowledge, such components have not previously been reported from studies of the coal → humic acid conversion and now raise the question of whether they are intermediates in the reaction sequence leading to humic acids or merely the result of dehydration of already formed humic acids. Because the answer to this question would provide experimental evidence for or against Tronov's postulates (17), suggesting that such cyclic anhydrides might be essential steps in the mechanism of conversion, a study pertaining to this problem is currently in progress in these laboratories.

Finally, some significance may be attached to the variations of carbon and hydrogen contents (cf. Figure 7a). The approach of these quantities to limiting values which cannot, apparently, be lowered by extending the reaction period, lends interesting experimental support to Francis' work on "oxidation tracks" and tends to validate the "limiting oxidation line" of his diagram (18). Prolonged oxidation, increased reaction temperatures, and/or higher oxygen concentrations appear to accomplish little more than conversion of carbon and hydrogen to CO_2 and H_2O respectively.

In the light of Figure 7a and b, it is obvious that optimum conditions for oxidation of a given coal, and for the production of a humic acid possessing predetermined properties, can be chosen with some ease. It is, however, equally obvious that artificial production of humic acids is subject to several limitations which arise as much from the meta-stability of humic acids as from the relatively low reaction rates. If it is accepted that humic acids hold an industrially important potential, further studies of their formation from coal are therefore imperative.

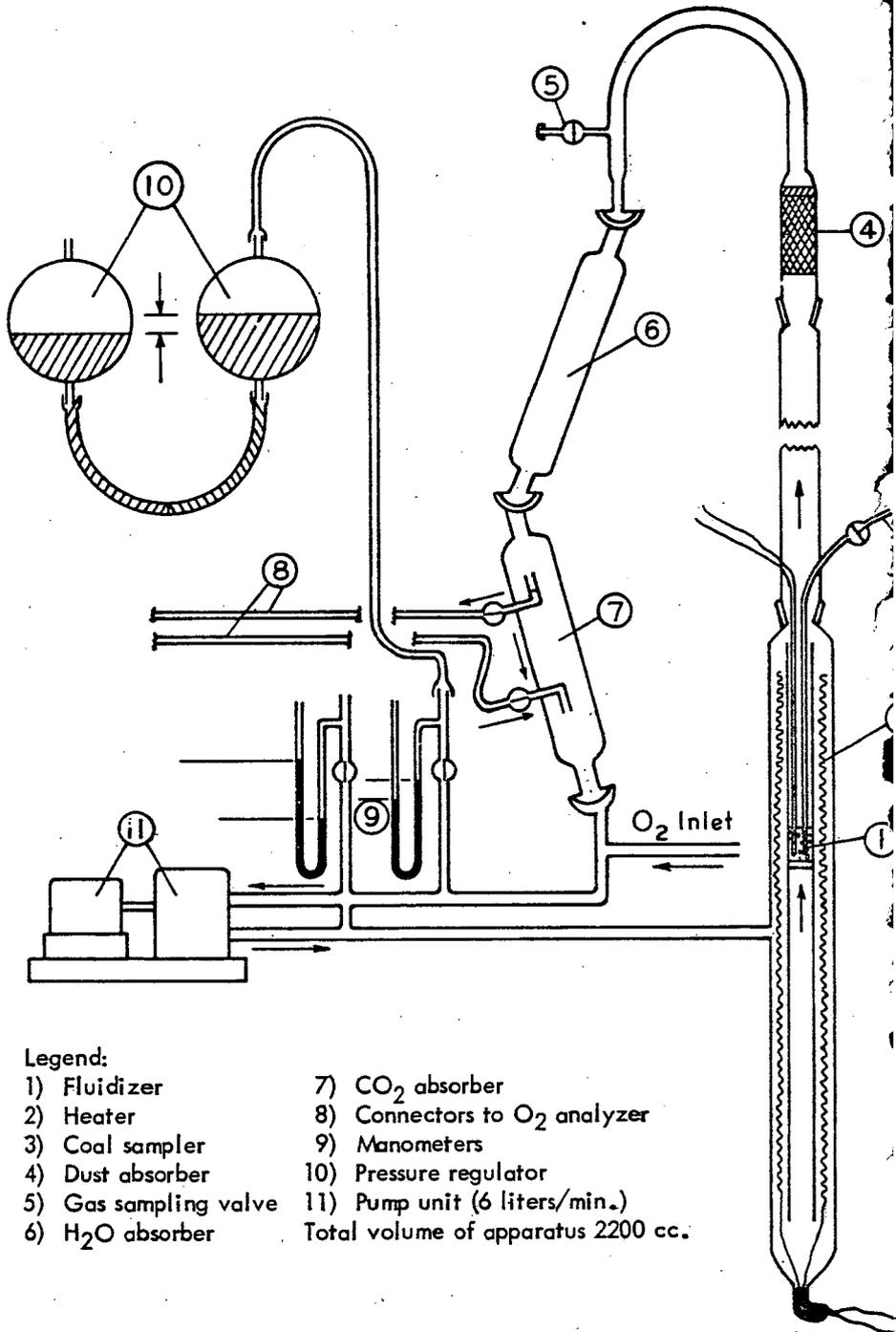
Acknowledgements

We are indebted to Dr. J. C. Wood for assistance in various phases of the experimental work (and particularly for his help in interpreting the infrared spectra) and also wish to thank Mr. J. F. Fryer for the analytical data and Mr. E. Kyto for help and inventiveness during the design and construction of the apparatus.

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FIGURE 1

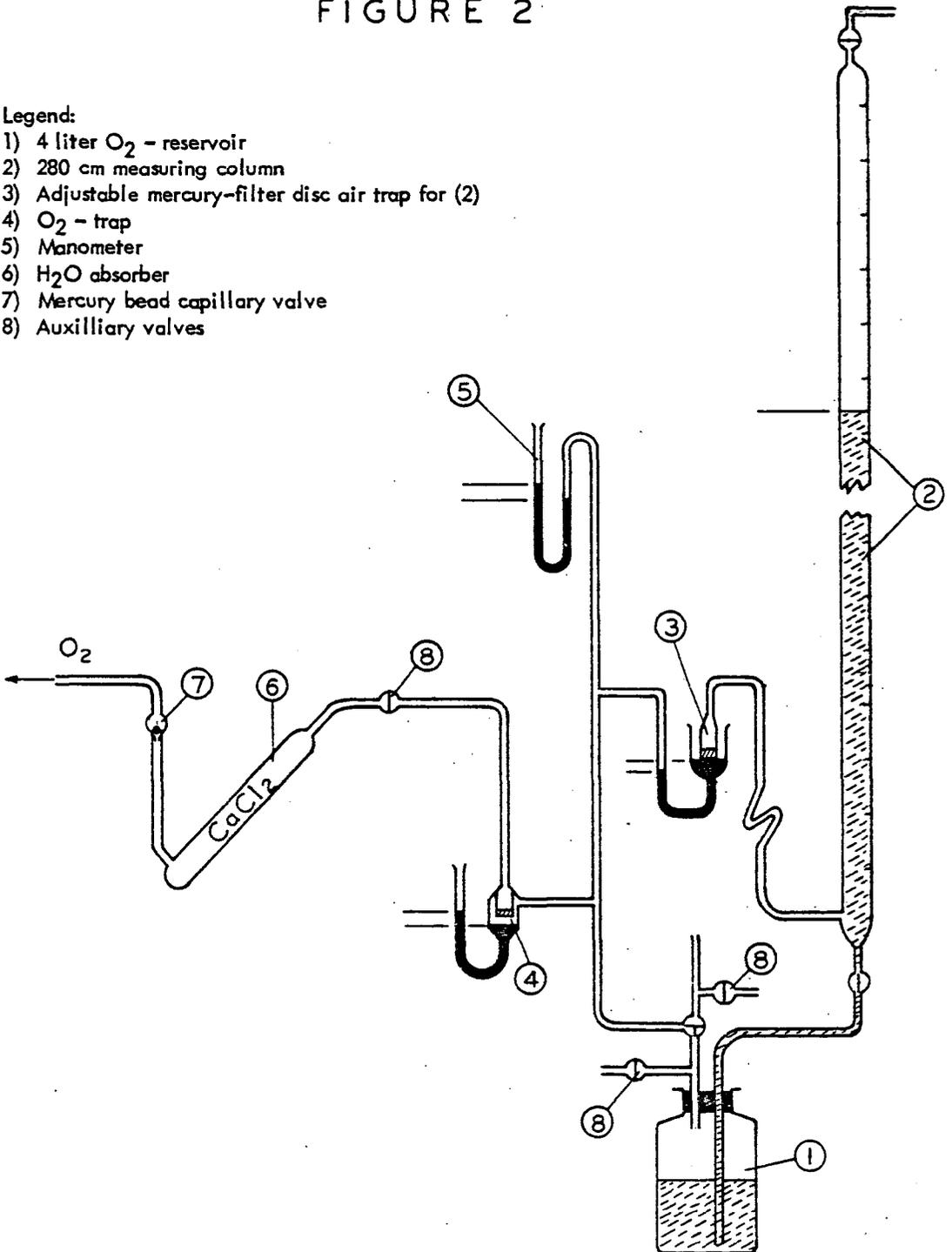


COAL OXIDATION APPARATUS
(not to scale)

FIGURE 2

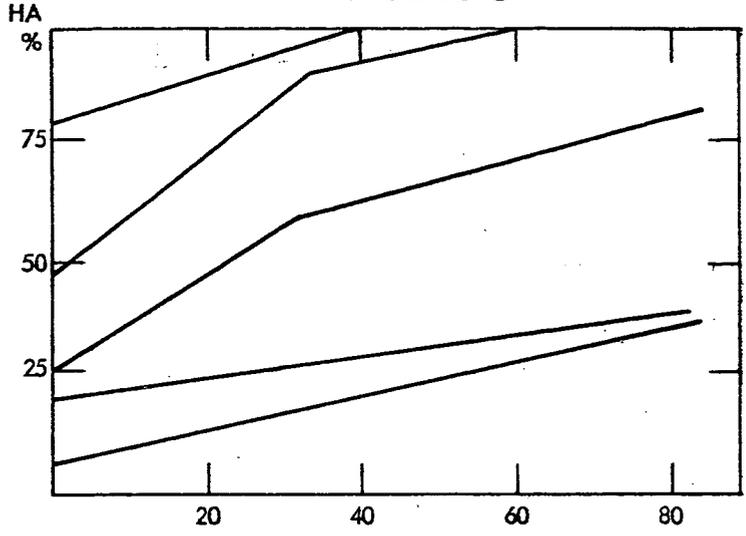
Legend:

- 1) 4 liter O_2 - reservoir
- 2) 280 cm measuring column
- 3) Adjustable mercury-filter disc air trap for (2)
- 4) O_2 - trap
- 5) Manometer
- 6) H_2O absorber
- 7) Mercury bead capillary valve
- 8) Auxilliary valves



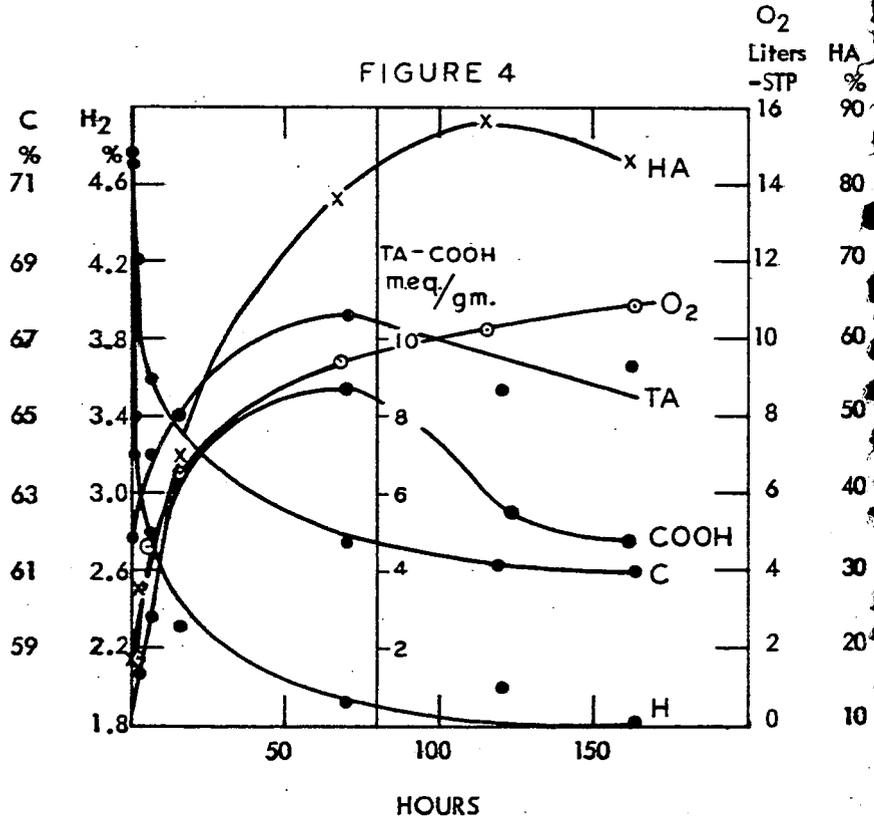
OXYGEN SUPPLY APPARATUS
(not to scale)

FIGURE 3

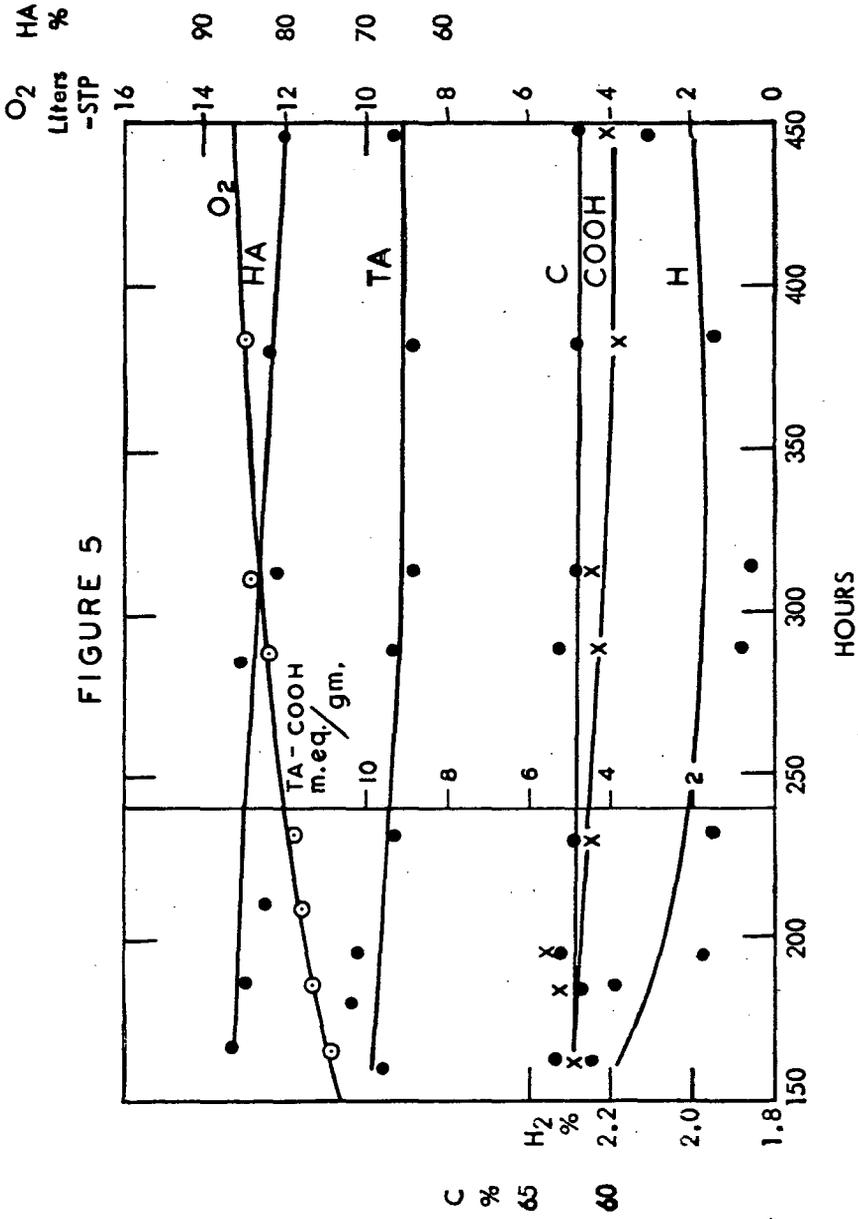


Titration of humic acid content. Changes of titre with time

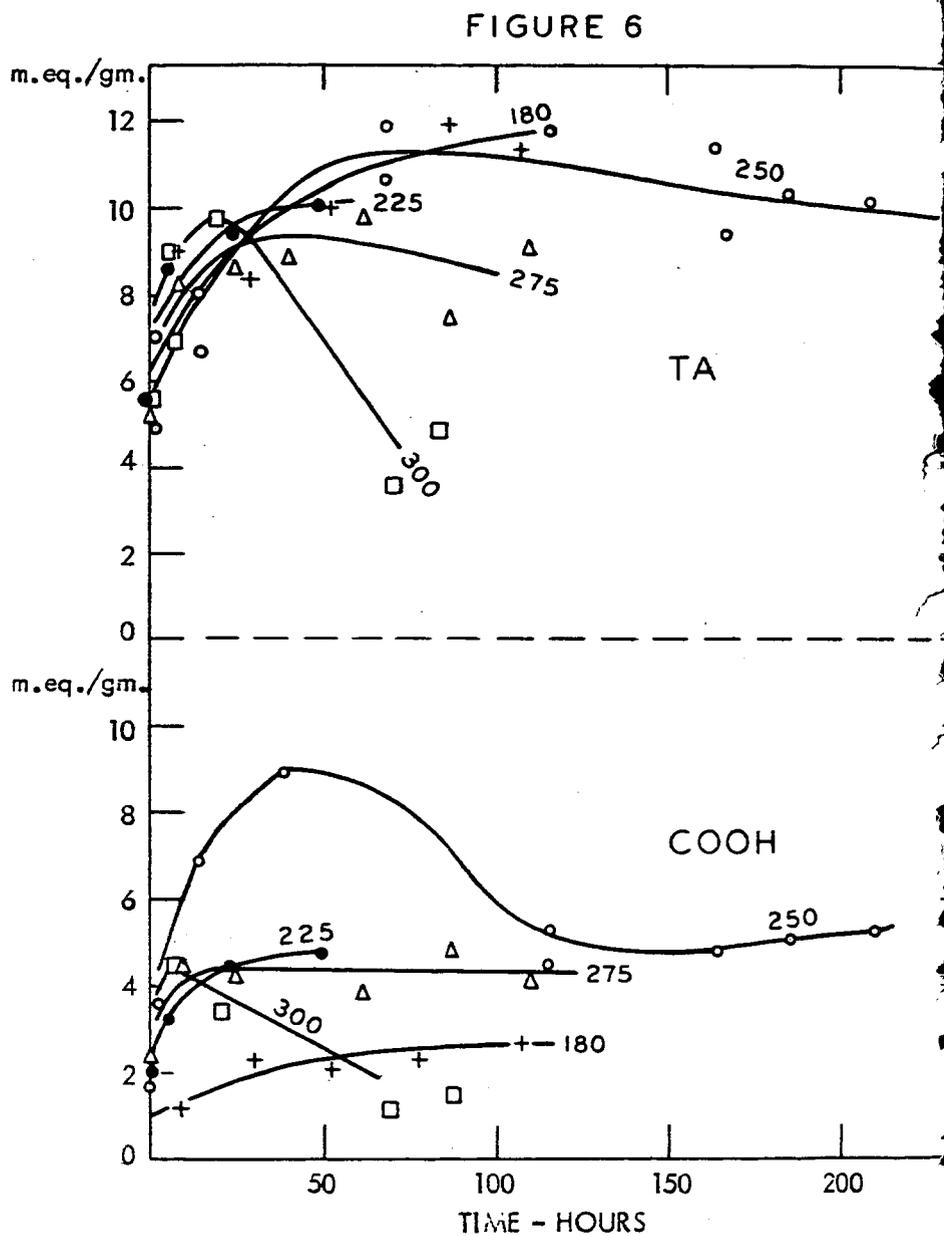
FIGURE 4



Variations of humic acid content and properties with time
 Legend: HA = humic acid content in % of sample, TA = total acidity, COOH = carboxyl, C = carbon, H = hydrogen, O₂ = oxygen consumption

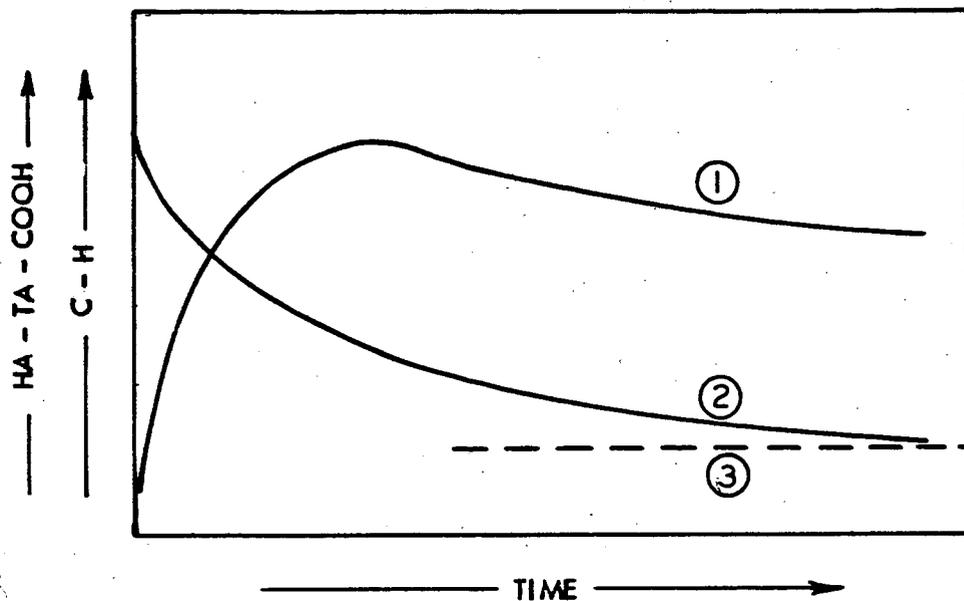


Variations in humic acid content and properties with time. Legend as in Figure 4



Variations in functional group content with temperature

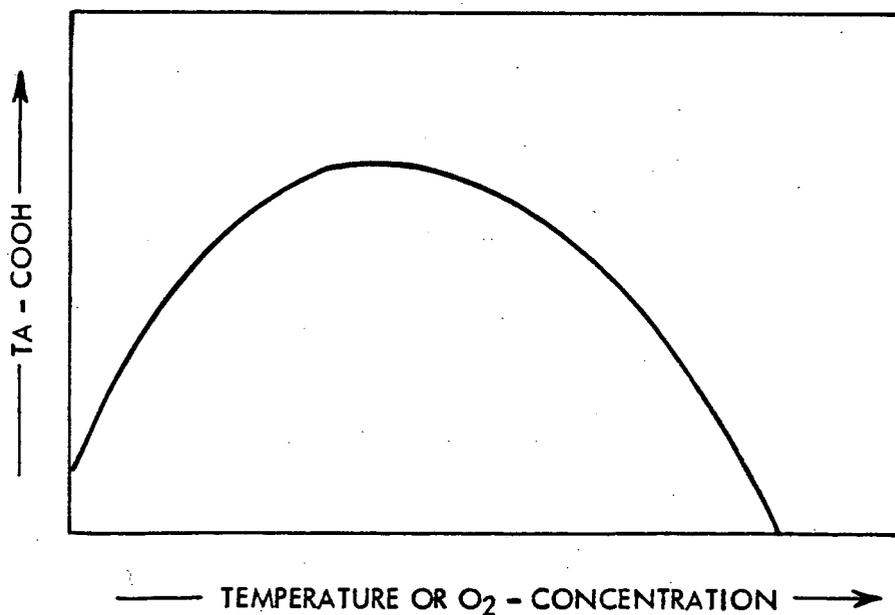
FIGURE 7 a



Variations of humic acid content and properties with time.

1) HA - COOH - TA 2) C - H 3) C - H limits

FIGURE 7 b



Variations in functional groups with temperature or O₂ - concentration

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Peat can roughly be defined as the product resulting from a special arrested decay of dead vegetation. The more typical pattern followed by dead plants is to undergo complete decay, with conversion of the organic matter into gases that are released into the atmosphere, while the inorganic matter remains in the soil. This complex process can take place only when the characteristic needs of the microorganisms that bring it about are met; these include, among others, air, water, and suitable nutrients. When dead plants accumulate under water, however, air is excluded and only a partial decay takes place, together with physical disintegration. After some hundreds of millions of years the successive products are lignite, then bituminous coal, and ultimately anthracite coal. But at a relatively very early stage, after some 10,000 to 20,000 years, the product of this arrested decay is peat. Peat, then, represents the bare beginning of the coalification process.

Considerable data have been published on the areas of peat bogs in various parts of the world, and on the amounts of peat in these bogs. It is probably safe to accept these data so far as they indicate orders of magnitude. Beyond this, they must be treated with considerable reserve, for the very good reason that virtually nowhere has the utilization of peat been great enough to justify the tremendous expense of an exhaustive accurate survey. (Two exceptions to this statement may be noted: first, in the Soviet Union and in Ireland, where there are large fuel peat industries; second, in any other area where there might be an exhaustive local survey for a specialty high-value peat, such as horticultural-grade sphagnum.) With these disclaimers, the following estimates are probably as good as any:

Table 1

World Peat Deposits¹

<u>Country</u>	<u>Square Miles</u>	<u>Country</u>	<u>Square Miles</u>
U.S.S.R.	65,000	Great Britain	9,400
Canada	37,000	Ireland	4,700
Finland	30,000	Newfoundland	3,000
Sweden	19,000	Norway	2,900
U.S.A.	11,200	Austria	1,500
Germany	9,900	Denmark	400

In addition, peat deposits are known to exist in the other continents, but there we cannot make even uneducated guesses.

Data on the amount of peat in the bogs are even less reliable than the bog areas, since the depths of peat deposits will vary over wide ranges; typically, from 4 to 20 feet within a given bog, and depths as shallow as

Page 2

a foot or two, and as deep as 50 feet or more, are not unknown. The following estimate, that of Kazakov,² again is presented only as an order of magnitude:

Table 2
World Peat Reserves²

	Billions of Tons ^a	
U.S.S.R.		153
Rest of world		
Europe (except U.S.S.R.)	24.8	
North America	18.1	
All others	27.1	<u>70</u>
World total		223

(a) On an air-dried (30% moisture) basis

And for the United States, we have the data of Soper and Osborn:³

Table 3
United States Peat Reserves³

State	Peat Area, millions of acres	Peat, millions of tons, air- dried basis
Minnesota	5.2	6,835
Wisconsin	1.0	2,500
Florida	—	2,000
Michigan	—	1,000
Virginia - North Carolina	—	700
New York	0.8	480
Maine	—	100
California	0.06	72
Ohio	0.05	50
All others	—	<u>90</u>
Total		13,827

Data on current production are presented in Table 4. The discrepancies between the sums of the values for individual countries and the totals at the bottom are due to the fact that the values in the table are based on data from two different sources,^{4,5} and some of the values are estimates by this author in an attempt to reconcile these sources. Only the larger producers are listed.

Table 4

World Peat Production in 1960

Country	Thousands of Tons		Sum
	Fuel	Nonfuel	
U.S.S.R.	59,100	86,000 (est.)	145,000 (est.)
Ireland	4,510	14	4,530
West Germany	871	895	1,780
East Germany	—	—	550
Netherlands	—	—	500
U.S.A.	none	471	471
Sweden	275	70	345
Norway	198	42	240
Denmark	—	—	187
Canada	negligible	185	185
Finland	132	6	138
Poland	—	—	125
Total (estimates) ⁵	60,000	100,000	160,000

A few conclusions are immediately evident from these data. First, with some 90 per cent of world production, Russia is by an overwhelming margin the largest factor in the world peat industry. Second, only in Russia and in Ireland does power from peat make up a substantial fraction of the national energy supply. Third, since nearly all the "nonfuel" use is in agriculture, world consumption of peat in agriculture is apparently greater than the amount burned for fuel. ("Apparently" because Russian data on nonfuel utilization are much less complete and up-to-date than their fuel data, and were here estimated by extrapolation.) Finally, in this country peat utilization is synonymous with agricultural utilization. Before going into this, it might be useful to describe the various types of peat.

While peats are classified by soils scientists into some half-dozen or more well-defined groups, commercial statistics⁶ are generally based on the following three classes:

Moss peat, or sphagnum peat moss, is peat derived largely from sphagnum and hypnum mosses. This is a light-colored material, springy, with a well-defined layered structure in its natural state. It is the least decomposed of the peats, with the lowest bulk density (7-15 lb./cu. ft.), the lowest ash content (usually under 4 per cent), the lowest pH (typically 3.5 to 5.0), and the highest moisture-holding capacity—up to 20 times and more its own weight of water. Virtually all peat imported into the United

States consists of sphagnum, which commands a much higher price than the other varieties.

Reed-sedge peats are peats derived from reeds, sedges, grasses, cat-tails, and various shrubs. They are much more decomposed and disintegrated than sphagnum peats, have a higher bulk density (20-35 lb./cu. ft.), are usually dark in color, and tend to have a fibrous structure that is due to their content of relatively undecomposed stems and roots. The pH range is 4.5 to 7.0; the ash content will typically vary from about 4 to 15 per cent but may be a good deal higher; and the moisture-holding capacity is about one-half that of sphagnum. About one-half to two-thirds of the peat produced in this country is reed-sedge.

Humus is a catch-all name for peats so completely decomposed and/or disintegrated as to have lost their biological identity. Humus may be native peat, or it may derive from peat land on which crops have been grown. The terms humus, muck, and peat soil tend to over-lap, but the ash content usually serves as a convenient if arbitrary dividing line between "true" peat--ash under 40 per cent--and peat soil--over 40 per cent. About one-third of United States domestic production can be classified as humus.

Although the nitrogen content of peat, some 1 to 3 per cent, is not negligible, this nitrogen is released so slowly that peat is not considered to have any particular value as a direct fertilizer. Its value in horticultural applications lies, rather, in its soil-improvement characteristics.^{7,8} The addition of peat to a heavy clay soil, for example, brings about a tremendous improvement in the structure of that soil. And the water-holding capacity of peat is beneficial to any soil, since peat tends to supply a buffer-type action: it will absorb excess moisture during periods of too-heavy rainfall, and release this water during drought periods, thus providing the growing plant with a more uniform supply of water. This is notably advantageous in sandy soils. These properties are particularly beneficial in the building of new lawns, for which large quantities of peat are mixed into the soil prior to the application of seed or sod. For similar reasons, peat is widely used as a mulching agent for ornamental plants and shrubs.

In addition to the major use just described for soil improvement, peat is used in a variety of other ways relating to agriculture. Potting soils, widely marketed in small plastic bags, are generally mixtures of peat and soil. Mushroom growers have been using peat for mushroom beds, and this practice appears to be growing.⁹ A relatively new outlet for peat is found in the small molded peat pots now sold in most garden supply stores. These were first developed in Norway, and substantial amounts of Norwegian pots are marketed in this country. More recently, several American producers have begun to manufacture these pots from domestic peats. And similar pots are now being made in Ireland on a different principle. Unlike

the Norwegian and American pots, which involve a high pressure molding operation, the Irish pot is made by cutting a suitable cavity in a block of air-dried peat. This preserves the original structure and porosity of the peat, and it is claimed that the greater cost of production is justified by the superiority of the product.

Another quite recent development shows particular promise. As the culmination of work extending over more than a decade, Baker¹⁰ and his colleagues developed the "U.C." formulas for nursery soil mixes, consisting essentially of mixtures of peat moss and fine sand to which suitable nutrients are added. This has attracted widespread and favorable interest. For example, the Irish national peat establishment, Bord na Mona,¹¹ has developed a modification of the U.C. formula adapted to European conditions, and is now marketing this material as the U.C.E.E. seed and potting compost.

Several older agricultural applications still account for substantial quantities of peat consumption. One of these is the use of peat for animal bedding and poultry litter. Its high moisture capacity makes the peat particularly suitable for this purpose, and the exhausted product consists of fine manure whose value is greatly enhanced by the soil-conditioning property of the peat with which it is combined. Another well-established utilization consists of the addition of 5 to 10 per cent peat to manufactured fertilizers. This is based on the fact that some of the components of commercial fertilizers are hygroscopic, so would become sticky in humid weather and hard-caked under dry conditions. By absorbing or releasing moisture as needed, the peat tends to keep the fertilizer free-flowing. Still another application of the moisture-holding property of peat is found in its use in the packaging of cut flowers and certain vegetables. Asparagus crates, for example, are sometimes lined with a layer of peat which is then wetted. By slowly releasing its moisture, the peat maintains the asparagus in good condition during shipment.

The one agricultural use which may ultimately have the greatest potential of all would be to incorporate into peat, by chemical or microbiological means, suitable plant nutrients in the right proportions and with the necessary characteristics of availability and rate of release, such as to add fertilizer properties to the soil-conditioning activity which peat already possesses. Needless to say, this problem has been and is being given energetic study in almost every laboratory where peat is looked at from a chemical or engineering point of view. Equally needless to say, the fact that a major industry of this nature does not exist indicates that the problem is still quite far from a solution. Nevertheless, two operations are in existence today in which such a peat-fertilizer-soil-conditioner is being produced. One is in Austria,^{12, 13} where the Österreichische Stickstoffwerke A. G. produces two peat derivatives of this nature--Humon and Voll-Humon. Humon is made by the reaction of air-dried peat (40% moisture) with anhydrous

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ammonia in the presence of air, at atmospheric pressure. The ammonia is completely absorbed in one pass with virtually no loss. This process raises the nitrogen content from about 1 to 3 per cent. The important consideration is the rate of release of nitrogen—about one-half becoming available the first year and the remainder within two years. The nitrogen content of the product is deliberately kept down to 3 per cent in order that as much humic material per unit of nitrogen as possible be supplied to the plant. The essential difference between Humon and Voll-Humon ("Complete Humon") is that the latter contains, in addition to nitrogen, the nutrients potassium and phosphorus, together with certain trace elements. A major problem with Humon and Voll-Humon appears to be that the cost of production still makes these products too expensive for ordinary agricultural use and thus limits their market to horticultural applications. Nevertheless, about 10,000 tons per year were being produced in 1957.

A related process is the one developed by the French company, Societe de Produits Chimiques et Engrais d'Auby.^{12,13} The process involves a fermentation of peat following a treatment with ammonia and other chemicals. Here, too, the cost of the product appears to present the major obstacle to widespread utilization of the process. Annual production was said to have been about 100,000 tons before the Algerian war destroyed a major part of the market.

Before we turn to nonfuel uses other than agriculture, which are found only outside the United States, a few statistics on United States production and consumption may be in order.

Table 5
United States Peat Consumption¹⁴

	Total Consumption, Thousands of Tons	Domestic Production			Imports	
		Thou- sands of tons	Value, Thou- sands of Dollars	Domes- tic Pro- ducers	Thou- sands of tons	Value, Thou- sands of Dollars
1939	134	55	362	39	79	1,204
1946	225	141	1,006	59	84	2,704
1950	255	131	1,143	48	124	3,867
1955	503	274	2,283	82	229	9,262
1958	597	328	3,446	81	269	12,034
1959	706	419	4,372	105	287	13,580
1960	735	471	5,138	115	264	13,509
1961	777	525	4,991	123	252	13,178

A few trends become apparent from these statistics. First, the use

of peat has shown a steady increase in this country with no sign yet of levelling off. This is understandable—we have become a nation of homeowners, and every lawn and every garden represents a new market for peat. Second, while domestic production shows a steady increase paralleling consumption, imports seem to have reached a maximum and leveled off. What is really surprising is the dollar value of the domestic product compared with that of the imported. In 1961, for example, we find 525,000 tons of domestic valued at about 5 million dollars, for an average of slightly less than \$10 per ton, as compared with an average value of the imports of over \$50 per ton—5 times as great. Two factors are involved. In the first place, the domestic prices reflect the proceeds received by the original producer f.o.b. plant, and frequently are for a product shipped in bulk. The imported prices are those paid by the importer p.o.e., and invariably include the cost of a rather expensive package. Nevertheless, there remains a considerable spread, and this is due to the fact that nearly all the imported material is peat moss, which commands a much higher market price than reed-sedge and humus, of which most domestic production consists. In fact, the major reason that imports are so high is that only a very small proportion of American peat deposits are sphagnum moss of suitable size and quality for commercial operation.

The next table shows, for the year 1960, the major sources of the peat consumed in the United States and the major outlets. The discrepancy between supply and utilization is due to the fact that only the material sold in commercial channels is listed in the consumption, with no account taken of peat utilized in captive operations.

Table 6

Peat in the United States—1960¹⁴

<u>Major Domestic Sources</u>	<u>Thousands of Tons</u>
Michigan	214
Florida	39
California	33
Pennsylvania	31
Washington	28
Indiana	27
New Jersey	25
39 Other states	less than 10 each
<u>Major Foreign Sources</u>	
Canada	157
West Germany	84
Poland	8
Netherlands	8
Denmark	6

Table 6 (continued)

<u>Major Uses</u>	<u>Thousands of Tons</u>
Soil Improvement	405
Potting Soils and Flower Packings	17
Miscellaneous	9

The nonfuel uses of peat outside of agriculture account for only a minor fraction of total peat consumption. On the other hand, one of them constitutes an important basic industry, and several show considerable interest and promise.

Perhaps the most important of these nonfuel nonagriculture applications of peat is its use as the raw material for the manufacture of activated carbon. The importance of activated carbon in sugar refining, gas purification, chemical processing, and other industries is well known. At least one of the major producers (Norit Co., Amsterdam)¹² makes most of its activated carbon from peat, and there are indications that others may follow suit. A serious limitation lies in the rather stringent specifications of the starting material. The nature of the (secret) process is such that the peat must be quite decomposed, to the extent that it sticks together like a damp mud when pressed by hand. At the same time, its ash content must not exceed about 3 per cent. So far as the writer knows, only one particular peat--a bog at the Holland-Germany border--has this combination of properties. The only low-ash American and Canadian peats are sphagnums, very little decomposed, and the ash content of the well-decomposed peats is rarely as low as even 6 per cent.

Since cellulosic substances constitute one of the major organic constituents of peat (15 to 50 per cent), the fermentation of peat to produce ethanol is a well-known process. However, it is not competitive with ethanol by other processes. On the other hand, the Russians^{12, 15} have developed a thermo-chemical processing of peat that at least in the Soviet economy is competitive. In this process the peat, only partially dried, is autoclaved with steam to destroy its colloidal structure. This makes it possible to dewater the peat by filtration, a process which the colloidal nature of untreated peat renders impossible. The process is therefore called "artificial dehydration." Some chemical products are produced during the autoclaving, and others during a subsequent fermentation, with the following overall yields from 1000 kg. of peat (37 per cent moisture basis): 6-8 liters of ethanol, 3.5-4 kg. of furfural and substituted furfurals, 700-750 kg. of peat fuel. Modifications under development would add 22-24 kg. of oxalic acid and 5-6 kg. of acetic acid to the above products. In 1957, a plant near Leningrad was operating at an annual peat consumption rate of 50,000 tons.

Processes for using peat for the manufacture of products such as wallboard, heat insulating plates, sound-proofing materials, and even papers and fabrics, are well known, and many patents have been issued. With suitable additives, these products can be made fire resistant. Before World War II the Soviets were known¹⁵ to produce heat insulating plates from peat on a large scale, but no current information is available. A related product from peat is a flooring material of rather high quality, which has been manufactured at various times in Sweden, Germany, and Russia, and probably elsewhere. And in the same category we find peat used as a filler in linoleum.

Wax constitutes another of the major organic constituents of peat (5 to 15 per cent), and the extraction of waxes from peat has been widely studied (Reilly, Ireland; Dragunov, Russia; Sundgren, Finland; Risi, Quebec). These waxes are comparable to the montan waxes from brown coal, and can be refined to a product comparable to Brazilian carnauba wax. But whether peat wax is competitive with these products remains to be seen.

A recent (1961) peat development that shows great promise is based on some work by the British Cast Iron Research Association,¹⁶ who found that the substitution of a particular type of peat for the coal dust or wood flour ordinarily used in iron foundry casting sands affords an improved product requiring less finishing. Current annual production of "Berkcoal," the trade name for peat meeting specifications for this purpose, is of the order of 12,000 tons.

Two minor uses of peat may deserve mention. During World War I, sphagnum moss was used on a large scale as a filler for surgical dressings and mattresses, an application based on its absorptive and antiseptic properties. And today in Germany, there are a large number of health spas whose major attraction consists of taking baths in a hot peat-water slurry. These are elaborate establishments, usually with one or even several physicians in full-time residence. The writer has no information as to how effective these peat baths are medically, but since the spa is usually located in beautiful mountain country far from the cares of everyday life, the overall effect is undoubtedly all to the good.

A final topic that should at least be mentioned is the use of peat lands for growing crops--either on native bogs, or on reclaimed peat land after removal of the peat. As an example of the first, suitably developed muck soils are highly regarded for crops such as celery and potatoes, while reclaimed bog lands are ideal for blueberries and cranberries. It should be emphasized, however, that the effective use of peat lands constitutes one of the major problems of soils scientists, particularly in the countries of Western Europe where arable land is scarce and precious, and that full realization of the potentialities of these lands still lies far in the future.

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MOLECULAR SIEVE PROPERTIES OF ACTIVATED ANTHRACITE

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It is well known that coals exhibit molecular-sieve properties. Such properties are characterized by much higher $n\text{-C}_4\text{H}_{10}$ adsorption than $\text{iso-C}_4\text{H}_{10}$ adsorption at room temperature (1) and particularly by activated adsorption of N_2 and A at 77°K . (1, 2, 3, 4, 5). However, this molecular-sieve behavior in the case of raw coal is of little practical value, since the diffusion rate of the adsorbate into the pore system is usually very slow and the total adsorption capacity is usually very low.

There is an increasing interest and use, today, of molecular-sieve materials by the petroleum industry for the separation of straight from branched-chain hydrocarbons. Synthetic crystalline zeolites are being used almost exclusively for this purpose (6). Charcoals made from the pyrolysis of certain polymers show promise (7). In this paper, the possibilities of producing a suitable molecular-sieve material by the activation of anthracite is considered.

Experimental

Anthracite Used - A Pennsylvania anthracite, which was ground in a fluid energy mill to an average particle size of 6μ on a weight basis, was used in this study. The proximate analysis (air-dry basis) of the anthracite was: moisture, 1.2%; V. M., 8.2%; fixed C, 79.4%; and ash, 11.2%.

Devolatilization of the Anthracite - Prior to activation, the anthracite was devolatilized in a N_2 atmosphere at 950°C . for 6 hours. No attempt was made to analyze the product gases during devolatilization; but from previous studies on kinetics of volatile matter release from anthracite, most of the gas released was H_2 (8).

Activation of Anthracite - Because of the fine particle size of anthracite used, a down-flow fixed bed reactor was employed. The reactor, which was 2.25 in. i. d., 3.25 in. o. d., and 2 ft. long, was made of 10-18 steel tubing. The anthracite sample holder, which could be inserted into the reactor, was 304 stainless steel. Its dimensions were 1.87 in. i. d., 0.065 in. wall thickness, and 17 in. long. The bottom was perforated to allow for the passage of the gases. Gas mixing and preheater sections were present, before the reactor. The entire apparatus is described in detail elsewhere (9).

For a run, an oven dried sample of anthracite of known weight was placed in the sample holder. The sample was heated to activation temperature in N_2 and then reacted with a 90% CO_2 -10% CO gas mixture, at a total pressure of 1 atm. Following reaction, the sample was cooled in N_2 and the percentage burn-off measured from the loss in sample weight. Carbon monoxide was added to the inlet stream so that more uniform activation through the bed would occur. That is, it minimized the effect of small amounts of product CO strongly retarding the gasification reaction (10).

Apparatus to Measure Properties of Anthracite

Apparent density - The apparent density of the samples was determined by Hg displacement. A Hg porosimeter was used (11), in which the total pressure above the Hg was raised to 2,000 psi. At this pressure, Hg is forced into openings greater than ca. 1000 A. Therefore, it is expected that the voids between anthracite particles were completely filled. At the same time, the volume of Hg forced into pores above 1000 A. within the anthracite particles is thought to be negligible (12).

Helium density - Prior to the measurement, the samples were outgassed at 125°C. for 8 hours. The He densities were determined by the conventional method in which a measured quantity of He was expanded into a sample holder (held at 30°C.) of known volume containing a sample of known weight. A 30 min. period was found adequate to reach equilibrium.

Adsorption apparatus - A static adsorption apparatus of the typical design (13), containing Hg float valves, was used. All adsorption studies were conducted at $30 \pm 0.1^\circ\text{C}$. Prior to measuring the free space with He, the samples were outgassed at 250°C. for 7 hours. Because of the very slow diffusion of the hydrocarbon adsorbates into the raw and devolatilized anthracites, 24 hours was allowed to reach equilibrium for each adsorption point. For the activated samples, a one hour equilibration time was found sufficient. The adsorbates used, $n\text{-C}_4\text{H}_{10}$, $\text{iso-C}_4\text{H}_{10}$, and $\text{neo-C}_5\text{H}_{12}$, were obtained from the Matheson Co. and were of greater than 99.9% purity.

Results and Discussion

It was decided to activate anthracite of micron size in this study in order to attain the optimum in uniform particle activation and to decrease adsorption equilibration time to a minimum. Walker and co-workers (14) discuss the effect of particle size on non-uniformity of gasification. Kawahata and Walker (12) show that the specific pore volume of activated anthracite increases with decreasing particle size in the range 16 to 150 mesh.

Unfortunately, however, the handling of 6μ anthracite during activation proved to be a problem. Initially, activation in a fluid bed apparatus, which was previously used successfully to react 100x150 mesh anthracite (15), was attempted. Excessive carry-over of the anthracite from the reactor as a result of continuous agglomeration and de-agglomeration made the use of fluidization impractical. In the case of the down-flow fixed bed reactor which was used for activation, it became evident that channeling of the gas was a problem. This apparently resulted in non-uniform reaction through the bed. That is, from the total per cent burn-off and the change in apparent density of anthracite during a run, the fraction of activation which took place within the anthracite particle (as opposed to removing external volume and thereby decreasing particle size) could be estimated. For the seven activation runs made, the percentage of internal activation varied widely, up to 100%, with no trend being found with changing activation temperature between 750 and 840°C. Results for only the sample with 100% internal activation are given here, to show under the best conditions what type of molecular-sieve properties activated anthracite can have.

The activated sample to be considered here, was reacted at 840°C. for 23.5 hours to 34.8% burn-off. Figure 1 shows the isotherms for the adsorption

of hydrocarbons on this sample. The isotherms can be closely approximated by the Langmuir equation, from which monolayer adsorption volumes can be estimated. These volumes for the activated and raw anthracite are given in Table I. Monolayer volumes for the devolatilized anthracite are not given, since they were very small and could not be accurately measured. For $n\text{-C}_4\text{H}_{10}$ adsorption at a relative pressure of 0.3, the volume adsorbed on the devolatilized anthracite was roughly 10% of that adsorbed on the raw anthracite. This indicates significant closure and contraction of pores upon heating of the raw anthracite to 950°C . Such a result has been previously reported upon the heat treatment of bituminous chars to higher temperatures (16).

From Table I, it is seen that the area available to the hydrocarbons is sharply increased upon activation, as expected. Of more importance, is the fact that the adsorption rate is markedly increased and that wide differences in the pore area available to the hydrocarbons still exist.

Table II summarizes the results for the apparent and He densities and total open pore volume on a m.m.f.b. To place the density results on a m.m.f.b., the apparent and He density of the mineral matter in all samples was taken as 2.7 g./cc. (17). The total open pore volume is considered to be the volume in pores $< 1000 \text{ \AA}$. and $> 2.5 \text{ \AA}$. in diameter. The lower limit is set by the size of pore into which He can diffuse at a significant rate at 30°C . (18).

On the basis of these results, the nature of the molecular pore system in the anthracites can be clarified further. From Hg porosimeter data on anthracite activated to 38% burn-off, it has been shown that about 94% of the total open pore volume is located in pores $< 28 \text{ \AA}$. in diameter (12). According to the Kelvin equation, pores of up to ca. this diameter will be filled by the hydrocarbons studied at a relative pressure of 0.3. Therefore, the assumption is made that the volumes of hydrocarbon adsorbed at a relative pressure of 0.3 are located in pores between a lower limit (below which the hydrocarbon will not enter) and 1000 \AA . Then, by subtracting these pore volumes from the total open pore volume, distribution data in the molecular pore size range can be determined. In agreement with Breck and co-workers (19) and others, the minimum effective pore size into which a hydrocarbon can penetrate is taken as the diameter of the circumscribed circle of minimum cross-sectional area of the hydrocarbon molecule. These minimum dimensions are 4.9, 5.6, and 6.5 \AA . for $n\text{-C}_4\text{H}_{10}$, $\text{iso-C}_4\text{H}_{10}$, and $\text{neo-C}_5\text{H}_{12}$, respectively.

These results are summarized graphically in Figure 2. It is seen that even though the total open pore volume is increased on devolatilization (presumably by volatile matter release unblocking pores), the amount of pore volume available to $n\text{-C}_4\text{H}_{10}$ and larger hydrocarbons sharply decreases. Comparing the volume distributions for the raw with the activated anthracite, it is seen that in spite of a large increase in total pore volume upon activation, the pore volume between 2.5 and 4.9 \AA . has decreased. This would suggest that there is little pore volume below 4.9 \AA . to be opened up by additional burn-off of this anthracite. It is to be emphasized that the volume reported below a minimum effective pore size would be expected to increase with increasing adsorption temperature, because of activated diffusion and an increasing magnitude of vibration of the atoms around a pore opening.

It is of interest to compare the activated anthracite with Type A synthetic zeolite pellets for adsorption of $n\text{-C}_4\text{H}_{10}$ and $\text{iso-C}_4\text{H}_{10}$ (19). At room temperature, the 5A zeolite has a capacity of ca. 50 cc. $n\text{-C}_4\text{H}_{10}$ /g. (S.T.P.) and 2 cc. $\text{iso-C}_4\text{H}_{10}$ /g. It is thought that the adsorption of

iso-C₄H₁₀ primarily occurs on the clay binder holding the small zeolite particles together in the pellet. The ratio of gases adsorbed is ca. 25. In contrast, the activated anthracite has a capacity of ca. 110 cc. n-C₄H₁₀/g. (m.m.c.b.) and 40 cc. iso-C₄H₁₀/g. The ratio of gases adsorbed is ca. 2.8. Pelletizing the anthracite for use in fixed bed operations would be expected to lower both the adsorption capacities and separation ratio. It is obvious, then, that this activated anthracite sample does not show the sharp molecular sieve effect demonstrated by the zeolite. This is to be expected, since a range of molecular pore sizes is present in the raw and activated anthracite. Nevertheless, because of the relatively low cost of activated anthracite, it may have possible applications for rough separations in conjunction with zeolites.

Acknowledgment

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Table I

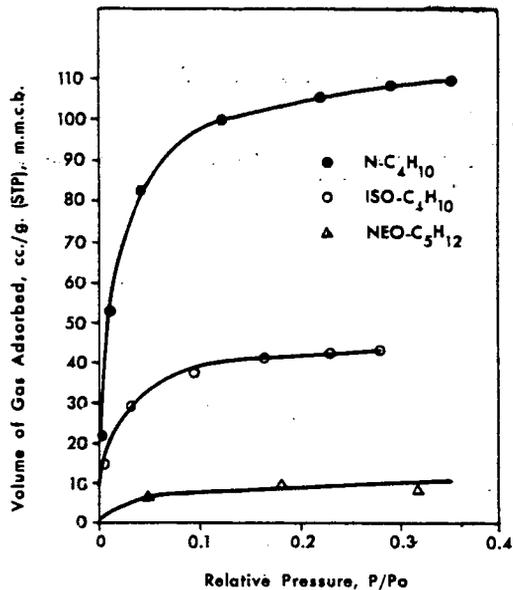
Monolayer Volumes for Different Hydrocarbons
 on Raw and Activated Anthracite (m.m.f.b)

	V_m , cc./g. (S.T.P.)		
	<u>n-C₄H₁₀</u>	<u>iso-C₄H₁₀</u>	<u>neo-C₅H₁₂</u>
Raw	12.6	8.6	2.3
Activated	134	54.5	15.5

Table II

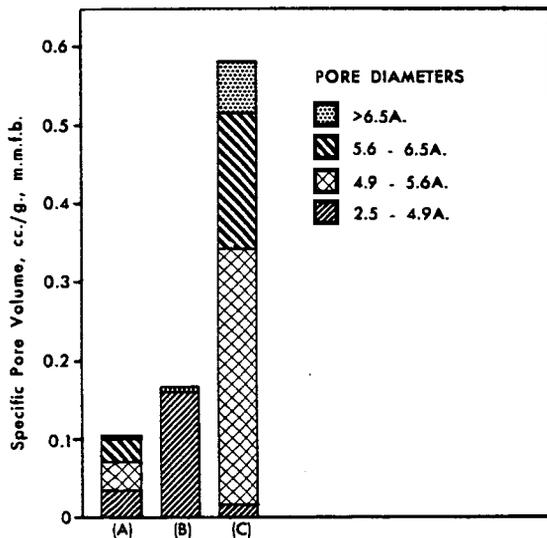
Densities and Total Open Pore Volume in Raw,
 Devolatilized, and Activated Anthracite (m.m.f.b.)

	<u>App. Density</u> g./cc.	<u>He Density</u> g./cc.	<u>Total Open Pore</u> <u>Volume cc./g.</u>
Raw	1.24 ₅	1.43 ₈	0.10 ₈
Devolatilized	1.51 ₀	2.01 ₀	0.16 ₅
Activated	0.95 ₇	2.15 ₆	0.58 ₁



HYDROCARBON ADSORPTION AT 30°C.
ON ANTHRACITE ACTIVATED TO 34.8%
BURN-OFF AT 840°C.

Figure 1



PORE VOLUME DISTRIBUTIONS IN RAW
(A), DEVOLATILIZED (B) AND ACTIVATED
(C) ANTHRACITES

Figure 2

Factors Affecting the Upgrading of Iron Oxide Derived From Fly Ash

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Introduction

The iron oxide present in fly ash can be removed by magnetic separation methods. The material so obtained has possible useful applications as a heavy media agent in coal preparation and as a raw material for the steel industry. In order to meet the various specifications of the materials now used in these processes, the fly ash-derived iron oxide must be further upgraded. This paper describes some of the problems encountered in upgrading the iron oxide material.

A. Separation of Iron Oxide from Fly Ash

Iron oxide can be removed from fly ash by either wet or dry magnetic methods. Typical magnetic separations systems which could be applied to this process are shown schematically in Figures 1 and 2.

The wet process (Figure 1) involves pumping a fly ash slurry into a unit containing a magnetic drum. The magnetic iron oxide and associated material are collected from the drum, and the collected material is passed through a similar unit for further refining. The non-magnetic material is transported to a disposal area.

The dry process also uses a rotating magnetic drum. The initial separation produces middlings and tailings fractions, which are discarded, and a crude iron oxide fraction which must be further refined by passing through another magnetic unit.

The iron oxide so obtained is similar in physical and chemical characteristics (Table 1) to commercially available magnetite and therefore can be used, in some cases, as a heavy media agent without further processing.

B. Processing of Iron Oxide for Use as a Heavy Media Agent

The important factor in the use of fly ash-derived iron oxide as a heavy media agent is the magnetic content of this material. The total magnetics should be as high as possible in order to have high recovery rates at the preparation plant, thereby keeping the consumption of iron oxide per ton of coal at a low rate.

Commercially available magnetite contains 94 percent magnetic material. Samples of iron oxide from fly ash can be produced containing 90 percent magnetics, however this requires further processing of the iron oxide in another magnetic unit, or alternately by crushing the iron oxide to liberate the magnetic material and subsequent magnetic separation to collect the magnetic fraction.

This latter process serves another purpose, namely, that of producing a finer sized material. Heavy media washers of different designs require magnetic material

of different size consists for efficient operation. Certain washers can use the fly ash-derived iron oxide as it is produced from the fly ash; others require a finer material. However, further grinding reduces the total magnetics content in the iron oxide. This occurs because non-magnetic materials are present in the iron oxide and are liberated by the grinding process. The reduction in total magnetics can be as much as several percent. Detailed comparison tests are yet to be made on this phase of the project.

C. Upgrading Iron Oxide for Use as a Raw Material in the Steel Industry

The object of this phase of the program was to refine the iron oxide to obtain a fraction having the highest possible iron content while maintaining a low silica and aluminum content. Considerable attention was therefore focused on the analysis of the iron oxide material. Methods of analysis were developed to determine iron, silicon and aluminum.

Several different refining procedures were attempted.

1. The iron oxide removed from the fly ash was pulverized until 90 percent passed a 325 mesh screen. The crushed material was then washed with water several times; after each washing the iron oxide was allowed to settle and the lighter material removed by decantation. This method did not increase the iron content nor did it decrease the silica content, however the aluminum content was reduced from 6.0 percent to 3.7 percent.

2. A second attempt at purification was attempted using the following method. The iron oxide was pulverized to 98 percent through a 325 mesh screen. The magnetic iron was removed by a dry magnetic method and then processed by specific gravity separations at 2.95 specific gravity. This method also did not improve the iron or silica contents, however it decreased the aluminum to 0.3 percent.

The results of these experiments showed that the iron and silica are intimately combined in such a form that grinding and washing will not make possible a separation. This combination is described as "silicated iron oxide" and has an iron-to-silica ratio of 4.6 to 1.

3. A third attempt at reducing the silica content was attempted. This method involved crushing the original, unprocessed fly ash to 98 percent through a 325 mesh screen, however when the resultant material did not yield any iron oxide when magnetic separations were attempted. The magnetic properties of the iron oxide apparently had disappeared.

These results led to a closer investigations of the physical and chemical characteristics of the fly ash.

D. Analysis of Iron Oxide for Iron Content

No standard wet analytical method for iron in fly ash was available for use in this work. Initially, the ASTM methods recommended for cement were used in which the iron was extracted from the fly ash by hydrochloric acid. From the color of, and microscopic examination of, the residues, it was suspected that all of the iron was not extracted by hydrochloric acid. Sodium carbonate and caustic fusions were attempted and gave higher results than the hydrochloric acid extraction (Table 2). However, it was again suspected that some of the iron had not been dissolved. Hydrofluoric acid extraction of the samples was then attempted and gave results which were consistently reproducible. The hydrofluoric acid extraction method gave the highest results.

It was believed that the problems with the analyses and processing of the fly ash-derived iron oxide were associated with the silicated iron material. Microscopic examination supported this belief.

Pollen amounts of (a) fly ash, (b) the residue from the magnetic separation process and (c) the magnetic iron oxide were examined and photographed under a microscope at 200 and 400 magnification using transmitted light.

Fly ash is formed at high temperatures during the combustion of pulverized coal. At these high temperatures, the ash forming constituents of the coal melt, fuse, and form spherical masses, in most cases (Figure 3).

The spherical particles containing iron oxide are essentially magnetic (Figure 4) and can be removed by magnetic processing.

Residues from the magnetic separation are essentially devoid of spherical iron bearing particles (Figure 5); however, a fair amount of iron oxide remains as ragged, irregularly-shaped particles, some of which have a cellular appearance (Figure 6). This material is believed to be thermally decomposed pyrite which had originally replaced fusain in the coal. This pyrite was thermally decomposed by the combustion process but did not fuse into the spherical mass which is typical of fly ash particles. This material may not be magnetic.

Examination of the magnetically separated iron oxide shows a great abundance of spherical particles, all of which are not pure iron oxide. Some of this material is the previously mentioned "silicated iron oxide". This silicated material appears to exist in two forms, one in which the magnetic iron oxide occurs as discrete particles imbedded in a spherical mass of silica (Figure 7), the other as a solid core of magnetic iron oxide surrounded by a siliceous mass (Figure 8).

While this material can be readily separated from the fly ash by magnetic methods, the associated siliceous material is also removed. This unfortunately is the major problem encountered in upgrading the iron oxide.

Future work on this project will be concerned with development of improved crushing and separation methods for upgrading the iron oxide to meet specifications for new, as well as existing, process applications.

Summary

Upgrading iron oxide derived from fly ash is complicated by the physical state of the iron as it occurs in the fly ash. The "silicated" state of the iron also presents problems in analysis. Ordinary crushing of the material to release the iron embedded in the silica has not been found to be an effective means to upgrade the iron oxide. The silica content remains unchanged and the magnetic content decreases. Further experimental work is necessary to achieve the desired degree of upgrading.

Acknowledgement

The photomicrographs were taken by Richard Moses, BCR petrographer.

TABLE 1. COMPARATIVE DATA ON FLY ASH-DERIVED IRON OXIDE AND COMMERCIAL MAGNETITE

<u>Screen Analysis - Percent Retained</u>		
<u>Screen Size</u>	<u>Iron Oxide</u>	<u>Commercial Magnetite Grade 2</u>
+ 50 mesh	0.15	3.8
50 x 70 mesh	0.25	4.4
70 x 100 mesh	0.70	4.4
100 x 140 mesh	0.35	6.2
140 x 200 mesh	6.35	7.6
200 x 325 mesh	26.80	13.5
- 325 mesh	62.40	64.5

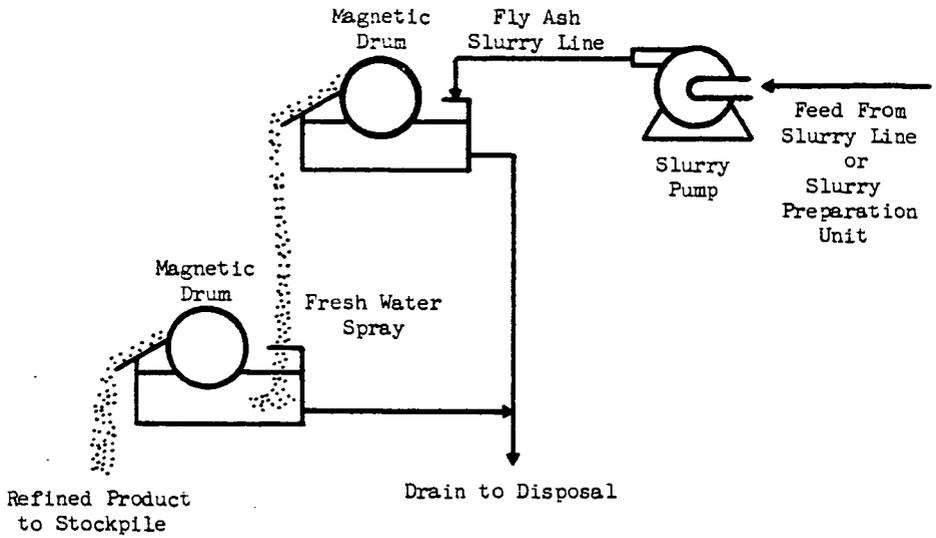
<u>Approximate Chemical Analysis, Percent by Weight</u>		
	<u>Iron Oxide</u>	<u>Commercial Magnetite</u>
Iron	57	62
Silicon	6	2
Manganese	0.8	0.2
Aluminum	3	4
Calcium	0.2	0.50
Magnesium	0.04	1.50
Moisture	0.10	0.50

<u>Physical Properties</u>		
Specific gravity	3.82	4.80
Magnetics	90%	94%

TABLE 2. COMPARISON OF RESULTS OF IRON ANALYSES USING VARIOUS METHODS

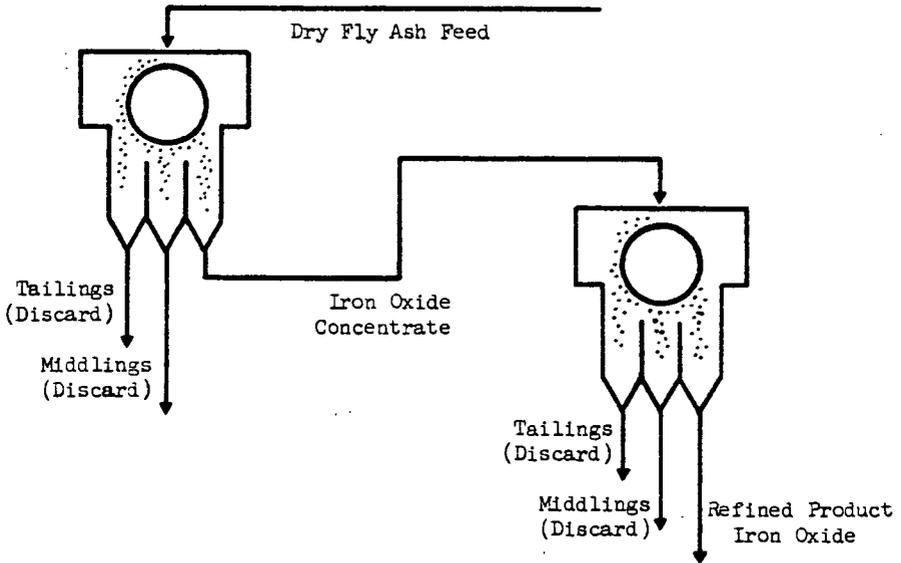
<u>Sample</u>	<u>Sodium Carbonate Fusion *</u> %	<u>Caustic Fusion</u>		<u>Hydrochloric Acid Extraction</u> %	<u>Hydrofluoric Acid Extraction</u> %
		<u>Initial</u> %	<u>Secondary</u> %		
1	5.9	8.7	-	6.0	11.6
2	14.9	11.0	14.9	3.2	18.4
3	4.5	5.7	-	2.7	8.0
4	4.6	8.1	-	7.2	11.1
5	36.8	36.7	4.5	41.3	44.1

* Results reported by another laboratory.



Bituminous Coal Research, Inc. 2508G1

Figure 1. Wet Magnetic Separation Process for Recovering Iron Oxide From Fly Ash



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Figure 2. Dry Magnetic Separation Process for Recovering Iron Oxide From Fly Ash

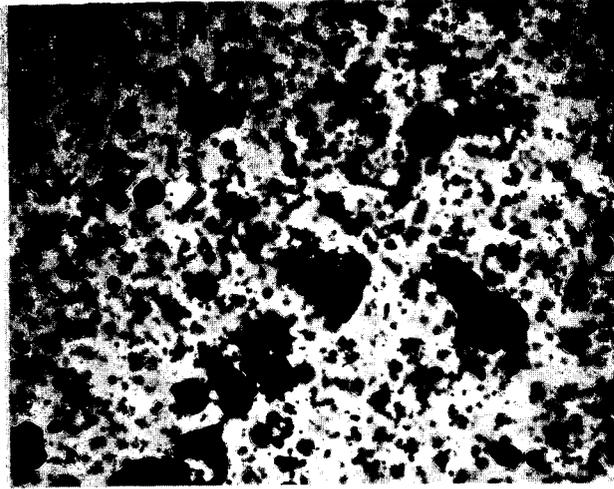


Figure 3. 2508P1
Fly Ash from Mechanical Dust Collector of an
Operating Power Station Burning Pulverized
Coal (200x)

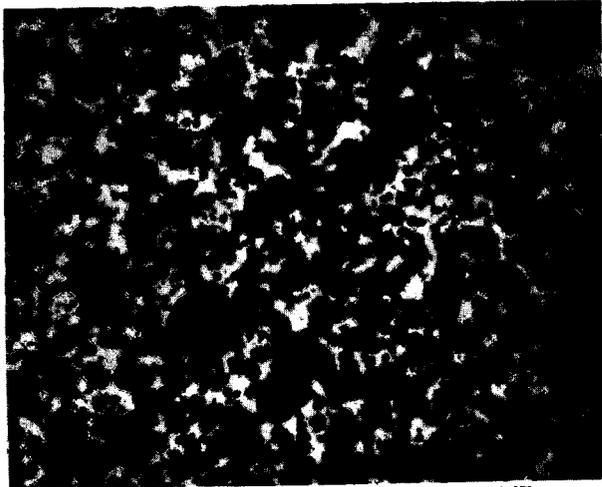


Figure 4. 2508P2
Iron Oxide Magnetically Separated from
Fly Ash (200x)

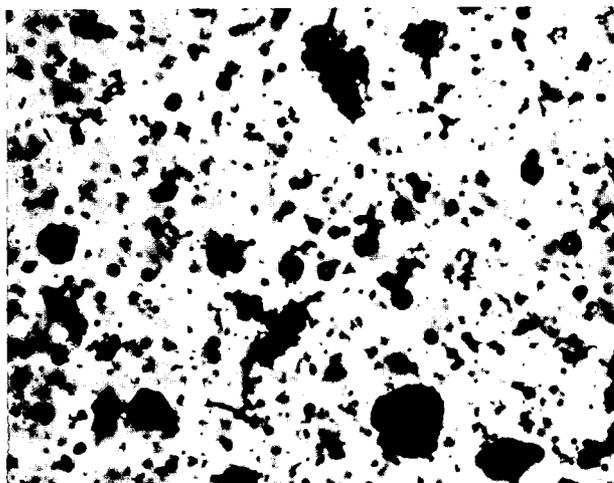


Figure 5. 2508P3
Non-Magnetic Residue from Magnetic Separation
of Fly Ash (200x)



Figure 6. 2508P4
Unfused Iron Oxide (top center) in Non-Magnetic
Fraction of Fly Ash (400x)

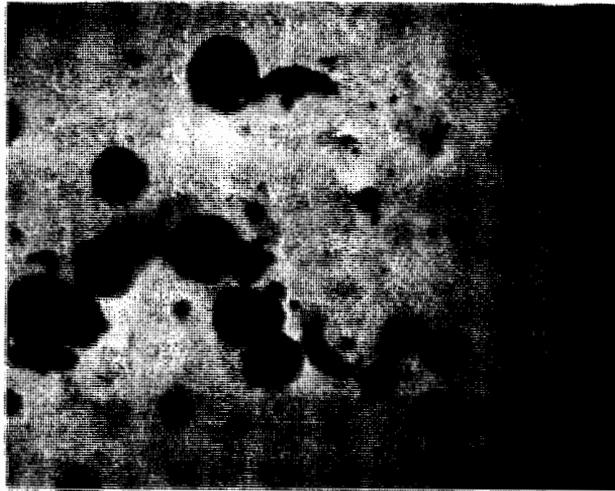


Figure 7. 2508P5
Discrete Iron Particles Enclosed in Siliceous Mass
Found in Magnetic Fraction of Fly Ash (200x)

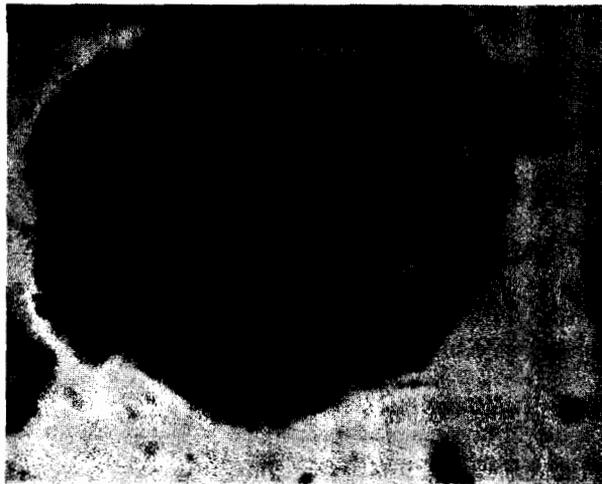


Figure 8. 2508P6
Iron Oxide Sphere Enclosed by Siliceous Mass Found
in Magnetic Fraction of Fly Ash (400x)

COAL-IN-TAR DISPERSIONS AS HIGHWAY CONSTRUCTION MATERIALS

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Introduction

When bituminous coal is digested in a mixture of coal tar pitch and high-boiling tar oil, at temperatures in the approximate range of 300-320 C., little or no chemical decomposition of the coal occurs and the coal-modified pitch, which appears to be a colloidal dispersion of the coal as coal in the pitch-oil mixture, has temperature susceptibility characteristics better than those of the original pitch, i. e., it softens less at elevated temperatures and hardens less as temperatures are decreased.

For about thirty years coal-modified pitches have been used very successfully as hot-applied enamels for the protection against corrosion of steel structures, marine piling and underground pipe lines for the transmission of oil, gas and water. Because of their superior temperature susceptibilities they are better for such purposes than coal tar enamels made by usual procedures.

Less successful have been various attempts to use coal-in-tar dispersions for other purposes for which it might be expected - because of their improved temperature susceptibilities - that they would be better than coal tar or asphaltic materials ordinarily used for such purposes. Of particular interest in this connection are some major efforts that have been made in Great Britain and, most recently, in South Africa and the United States to employ coal-modified tars as binders for bituminous highway pavements.

Bituminous Road Binders - Tar vs. Asphalt

Binders used in pavements of the bituminous concrete type are made either from petroleum, by the vacuum or steam reduction of petroleum residuals, or from coal tar by straight distillation to the required consistency or the fluxing of coal tar pitch with tar oils. In the United States unfilled hot-mix binders of petroleum origin are called asphalts, paving asphalts or asphalt cements whereas in Great Britain and various other countries they usually are referred to as bitumens, asphaltic bitumens or petroleum bitumens to distinguish them from natural or synthetic mixtures of bitumens and fillers that are called asphalts. In the following discussions unfilled asphaltic binders will be designated as paving asphalts or asphalt cements. Coal tar binders, made either by straight distillation or the fluxing of pitch with tar oils, will be designated as tar cements.

In general, asphalt cements have better temperature susceptibilities and are less volatile at mixing, paving and atmospheric temperatures than tar cements. On the other hand, tar cements have better adhesion to most road aggregates on prolonged contact with water; are more resistant to chemical alteration by water; are dissolved or softened less by petroleum lubricating oils, jet fuels and gasoline; produce more permanently skid resistant pavements and are not as susceptible to

56. age hardening within pavements that are densely graded or tightly sealed so that oxidation or evaporation of the binder is minimized.

Experience, both in the United States and abroad, has shown that excellent pavements of the bituminous concrete type can be constructed either with asphalt cements or with tar cements. However, different mixing and paving techniques are required. For example higher aggregate drying and mixing temperatures are needed when asphalt cements are used to insure substantially complete removal of all moisture from the aggregate and to fluidize the asphalt cement sufficiently to insure rapid and thorough coating of all aggregate particles. Lower temperatures should be used for tar cements to avoid excessive volatilization of tar oils with consequent hardening of the binder. With tar cements it is possible to use lower aggregate and mixing temperatures because they will tolerate considerably more moisture in the aggregate than asphalt cements. Also because tar cements are sufficiently fluid at the lower temperatures to insure satisfactory mixing and paving operations.

Another important difference in the preferred construction techniques for pavements containing tar or asphalt cements has to do with aggregate gradations. For best results, tar cements should be used with densely graded aggregates so that the finished pavements will be substantially voidless (3-5% residual air voids). Should a slight excess of tar binder in the mixture cause flushing of binder to the surface, the thin film of tar cement, on hardening, will be worn off by traffic. This will expose the angular particles of aggregate to produce a skid-resistant pavement surface. Because of the density of the compacted mixture, evaporation of oils from thin tar films below the pavement surface is prevented and little or no alteration of the tar binder occurs. On the other hand, a somewhat more open aggregate gradation may be used with asphalt binders. If sufficiently dense mixes are used so that flushing occurs, this must be held to a minimum to avoid the development of slippery surfaces when wet.

Methods For Improving Tar and Asphalt Binders

Various methods have been used or tried with a view to improving both tar and asphalt binders. In the case of asphalt cements such efforts have been directed mainly toward better adhesion to aggregates in the presence of water by the admixture of certain chemicals or tar oils, greater skid resistance by the addition of coal tar pitch and less "age hardening" through the use of better manufacturing procedures including the selection of raw materials.

Efforts to improve tar cements have been directed almost entirely toward the improvement of their temperature susceptibilities. The method most commonly employed, especially in Great Britain and Germany, has been the addition of paving asphalts to tar cements. Usually the asphalt content of such mixtures has been about 15 - 25 per cent but as high as 40 per cent has been used with some mid-temperature coal tars such as are produced by vertical retorts. In the latter case some improvement in binding capacity as well as temperature susceptibility is expected. As yet, this method has not been used extensively in the United States, largely because the asphalt cements produced in this country vary widely with respect to compatibility when mixed with tar cements derived from high-temperature, coke oven coal tars. When stored and used at the high temperatures employed at hot-mix paving plants such mixtures may or may not segregate or sludge depending upon the type of petroleum from which the asphalt was derived and the method of reduction used in its manufacture.

The addition of small amounts of synthetic rubber to coal tar cements is another method that has been used to some extent for improving their temperature susceptibilities. They have been used most extensively at airports where asphalt surfaces have been damaged excessively by jet fuel spillage. Aprons or runways constructed with rubberized tars, in addition to being jet-fuel resistant, deform less at high temperatures and are less likely to crack at low temperatures under heavy loads and impacts. However, the addition of rubber to the tar does not reduce its volatility and the rubberized tar binder must be stored and used at the lower temperatures recommended for usual tar cements.

Another possible method for improving tar cements is the one that will be reviewed in this paper, namely, coal-in-tar dispersion.

The Dispersion of Coal as Coal In Tars and Oils

The fact that coal as coal, at temperatures below those at which chemical decomposition of the coal begins, can be dissolved or colloiddally dispersed in cyclic hydrocarbons such as coal tar, water gas and oil gas tars, or chemicals, oils and pitches derived therefrom was recognized, almost forty years ago, by Harold J. Rose and William H. Hill. From investigations started about 1924 in the Mellon Institute laboratories of the Koppers Company, Pittsburgh, Pennsylvania, they found that at digestion temperatures preferably in the approximate range of 300 - 320 C, bituminous coal appears to dissolve in tars and tar oils, or their combinations, without chemical decomposition of the coal. The end product is a pitch-like material which, depending upon the kinds and proportions of ingredients used, may have temperature susceptibilities substantially better than those of pitches made from coal tar, water gas tar or oil gas tar by usual distillation procedures. Presumably, as the digestion product cools to atmospheric temperature, the coal, which had dissolved in the digestion medium at the digestion temperature, comes out of solution to form a gel-like, colloidal dispersion of the coal in which, except for insoluble mineral ash, no particles of the original lump or pulverized coal are visible with a microscope at magnifications of 400 - 500.

The laboratory investigations of Rose and Hill resulted in the issuance of several United States and foreign patents to them with assignment to The Koppers Company. Their first patent¹ of this kind was issued in Great Britain in 1928. The laboratory studies were followed by extensive pilot plant and field investigations in which the Research Division and the Tar Products Division of The Koppers Company collaborated. Many possible outlets for coal-in-tar dispersions were investigated but most successful was the development by Koppers of superior enamels and coatings for steel structures, marine piling and transmission pipe lines for oil, gas and water. Their superiority over other coatings used or proposed for use on buried pipe lines was established by service tests conducted jointly by The American Petroleum Institute², The American Gas Association and The U. S. Bureau of Standards. In those tests, which were started in 1930 and concluded ten years later, pipe nipples coated with the various test materials were buried at fourteen locations in the United States and specimens were inspected at yearly intervals. Koppers' coal-digestion product, designated as Komac, behaved so favorably that its commercial production was started by the Wailes, Dove, Hermiston Corporation, maker of Bitumastic enamels and coatings, following the disclosure of manufacturing procedures to them by Koppers. Other commercial uses for coal digestion products were tried, less successfully, by the Koppers Company but they did not include highway construction or maintenance materials, except for a few field tests that were made

58. with coal digestion pitches as brick and concrete pavement joint fillers. The first efforts to use coal-in-tar dispersions as road construction materials were made in Great Britain.

British Experiments with Coal-modified Tar Road Binders

In 1929 a British patent³ was issued to the South Metropolitan Gas Company, London, (Pickard and Stanier) on a process for making a tar product with improved "temperature-mobility" characteristics. As in the case of the British patent¹ issued to Rose and Hill (Koppers) in 1928 the process consisted in dispersing coal in tar at about 300 C but the South Metropolitan Gas Co. patent was directed specifically toward making an improved road material or a substitute for mixtures of tar and asphaltic bitumen (paving asphalt) for road-making and like purposes by dispersing not more than fifteen percent of bituminous coal in coal tar. Tar suitable for the purpose was made either by partial distillation of crude coal tar to drive off lighter oils which would be lost during the digestion process at approximately 300 C or by distillation of the crude coal tar to pitch and subsequent adjustment of the latter by the addition of tar oils.

A second British patent⁴ was issued to South Metropolitan Gas Company (Herbert Pickard) in 1930. It claimed the mixing with stone of a tar binder of the coal dispersion type described in the preceding patent to produce a road surfacing mixture of the hot-mix, hot-lay, asphaltic concrete type.

Detailed information gained from their investigations was furnished by Evans and Pickard in a treatise⁵ published by South Metropolitan Gas Company in 1931. It contained a large amount of valuable information about (1) The Relationship Between Temperature and Consistency of Coal Tar (2) The Preparation Of Asphaltic-Like Substances From Coal Tar and (3) The Consistency of Pitch-Like Substances.

According to personal communications recently received by the author, additional experiments involving the use of coal-in-tar dispersions were made in Great Britain in 1945 by the South Eastern Gas Board (formerly known as South Metropolitan Gas Company). As in the earlier experiments, the purpose of the tests was to substitute coal-in-tar dispersions for tar-asphalt blends for dense tar surfacings. Asphalt suitable for the purpose was expensive and in short supply at that time, but shortly thereafter it became more plentiful again and work on the coal dispersion binders was discontinued.

Also, according to personal communications, the Coal Tar Research Association of Great Britain made additional tests in 1956 that were directed toward the improvement of tar binders for use in dense surfacings on airfields. Coal was digested in a mixture of coal tar pitch and topped coke oven tar heavy oil. Laboratory tests were said to be encouraging but, when small test sections of pavement were laid, fuming was reported to be somewhat excessive and large scale service tests were not attempted.

Coal-Modified Tar Binder Experiments in South Africa

In a paper⁶ published in October 1959, Dr. H. Karius and Dr. E. J. Dickinson reported the results of investigations which they had conducted in Pretoria, South Africa as a part of the program of research of the Bituminous Binder Research Unit, National Institute for Road Research. The purpose of the work was "to find means of decreasing the temperature susceptibility of viscosity and the brittleness at low

temperatures of road tars derived from steel works coke-oven crudes at least to the level of that of straight-run petroleum bitumens". Concerning coal-in-tar dispersions, their observations may be summarized as follows:

1) Road binders with temperature susceptibilities of viscosity and brittleness at low temperatures similar to those of bitumen (asphalt) resulted from the digestion of certain types of South African coal in tar especially in concentrations of 10 - 15 percent by weight.

2) The combined effect of coal and synthetic rubber on tar or pitch is greater than the sum of their separate effects. With coal present, the amount of synthetic rubber needed to equal the flow characteristics of asphalt is minimized or, by dispersing both coal and synthetic rubber in tar or pitch, flow characteristics superior to those of asphalt are obtainable. However, when coal is present it is necessary to add a substantial amount of high-boiling coal tar oil to reduce the viscosity of the dispersion when it is to be used for road construction purposes.

3) Either the GR-S (styrene-butadiene copolymer) or the Buna N (butadiene-acrylonitrile) type of synthetic rubber may be used in conjunction with coal to improve the rheological properties of tar but the GR-S type must be added in latex form.

4) Synthetic rubber, especially of the Buna N variety, when added to pitch-asphalt mixtures, appeared from laboratory tests to act as a stabilizing agent so that any pitch-to-asphalt ratio might be used without causing incompatibility in the heated mixture. Also heat-stable pitch/oil/coal/asphalt/rubber blends were prepared by mixing a coal/pitch/oil blend with a rubber/asphalt blend. Both natural rubber latex and Buna N latex were used in this manner.

Heat stable blends of the types mentioned above were described in a South African patent application⁷ filed in June 1958 by Karius and Dickinson and assigned by them to the South African Council for Scientific and Industrial Research.

During and after the laboratory investigations of Karius and Dickinson, single-seal applications of tars and asphalts, with and without the addition of coal and polymers, were made on highways near Pretoria so that they might be compared and evaluated under actual service conditions. Reports on the outcome of those field tests have not yet been published.

American Investigations of Coal-Modified Tar Road Binders

Curtiss-Wright and Kentucky Highway Department Tests

The most recent attempt to develop improved binders for bituminous concrete pavements by the dispersion of coal in tars and oils was made in the United States. In the Fall of 1958 the Curtiss-Wright Corporation, whose research and development laboratories were located at Quehanna, Pennsylvania in the heart of a bituminous coal mining region, decided to explore this possibility after conferring with members of the U. S. Bureau of Mines, Bituminous Coal Research Inc. and others. Because of the successful use of coal-in-tar dispersions as pipe line enamels, which the Koppers Company was known to have developed following the researches of Rose and Hill, it was thought that similar techniques could be employed for the production of improved road binders.

Curtiss-Wright was aware of the early work along similar lines that was done by the South Metropolitan Gas Company in England but was not aware of the more recent experiments by the South Eastern Gas Board and by the Coal Tar Research Association in Great Britain or by Karius and Dickinson in South Africa.

Articles describing those investigations had not yet been published. In fact, nothing was found in the literature which would indicate that anyone had commercially produced satisfactory coal-modified tar binders for highway construction purposes.

Laboratory tests which began at Quehanna in January 1959 were continued, without interruption, for almost two years. During the latter half of 1959 they were supplemented by pilot plant and full scale highway service tests in Kentucky in which the Curtiss-Wright Corporation and the Kentucky State Highway Department collaborated. The laboratory work at Quehanna and also the design, construction and operation of the Kentucky pilot plant was, for the most part, directed by Mr. S. H. A. Young, Chief Development Engineer of the Curtiss-Wright Research and Development Department; the Project Leader at Quehanna during most of the two year period was John Horai; Frank Soriero was manager, for Curtiss-Wright, of the pilot plant and field operations in Kentucky and E. O. Rhodes assisted Curtiss-Wright in a consulting capacity both at Quehanna and in Kentucky. The Kentucky mixing and paving operations were supervised by the Highway Research Laboratory, Kentucky Department of Highways, of which Dean D. N. Terrell was the Director and Mr. W. B. Drake the Associate Director. An independent study and evaluation of the various binders produced and used in the Kentucky experiments was made in Washington, D. C. by The U.S. Bureau of Public Roads. The results of the Quehanna, Kentucky and Washington investigations were reported at the 41st annual meeting of the Highway Research Board, Washington, D. C. in January 1962 in preprints of papers by Rhodes⁸, Drake⁹, and Halstead, Oglie and Olsen¹⁰. Following is a condensed summary of the information furnished by Rhodes concerning the Quehanna and Kentucky experiments.

Preliminary Quehanna Investigations

During the first six months of 1959 many laboratory tests were performed by Curtiss-Wright at Quehanna, Pennsylvania in which coal dispersions were made with different coals, tars and oils under varying conditions of time, temperature and pressure. From a large number of formulations tried, two were selected for comparison with a typical 70-85 penetration asphalt cement and with a representative sample of tar cement meeting ASTM specifications for RT-12 grade road tar. The latter was made by straight distillation of high temperature, coke oven coal tar. One of the coal dispersions, (CW-II), contained 10.8% bituminous coal from the Freeport seam near Quehanna, Pa. and 89.2% of the RT-12 tar cement. The other (CW-III) contained 11.4% Freeport seam coal, 64.4% RT-12 tar cement and 24.2% high-boiling coal tar oil (m. m. t. 5% distillate to 315 C and 70-75% residue at 355 C). In each case the coal, dried and pulverized to pass 100% through a 100 mesh sieve, was mixed with the RT-12 road tar or RT-12 plus high-boiling coal tar oil, the mixture was heated, with agitation, to 600 F (315.5 C), maintained at that temperature for one hour, cooled to 400 F and withdrawn from the autoclave into containers. The autoclave was vented to the atmosphere throughout the run. Neither pressure nor reflux was required to obtain complete dispersion of the coal in the tar or mixture of tar and oil.

Laboratory tests indicated that each of the coal-modified tar cements (CW-II and CW-III) should be superior to the 70-85 penetration asphalt cement with respect to insolubility in jet fuels and also adhesion to aggregates in the presence of water; furthermore, it appeared that they should be superior to the RT-12 grade tar cement but somewhat inferior to the asphalt cement from the standpoint of volatility at usual asphalt mixing and paving temperatures. (225-325 F).

Comparative tests on Marshall briquets made with the various binders gave the following results:

Marshall stabilities at 140 F of briquets made with the coal-modified tar cements (CW-II and CW-III) were approximately 50% higher than those of the asphalt briquets and 100% higher than the stabilities of RT-12 briquets.

Immersion in water for 96 hours at 120 F caused the Marshall stabilities of briquets made with CW-II, CW-III and RT-12 to increase 9%, 88% and 14% respectively whereas the stabilities of the asphalt briquets decreased 17%.

After heating for 72 hours at 140 F the stabilities of briquets containing CW-III decreased only 3% and impact resistance at 32 F increased 32%. The stabilities of the asphalt briquets decreased 20% and their impact resistance at 32 F decreased 26%.

The jet fuel solubility of the CW-III briquets was only 2% as compared with 38% for the asphalt briquets.

The asphalt briquets were somewhat superior to those made with coal-modified tar binders with respect to impact resistance at 32 F and evaporation loss on heating for 72 hours at 140 F.

On the whole it appeared from the preliminary Quehanna experiments, that improved binders for bituminous concrete pavements could be made by the modification of a standard grade of coal tar cement (RT-12) with bituminous coal or bituminous coal and high boiling coal tar oil. Public announcements to the effect were made by Curtiss-Wright in April 1959 and shortly thereafter they contracted with the Commonwealth of Kentucky to produce 150,000 gallons of coal modified tar cement for experimental use in that state.

Kentucky Pilot Plant

A pilot plant to make 1500 gallon batches of coal-modified tar cement was designed by Curtiss-Wright and it was installed and operated by them at Frankfort, Kentucky during the latter half of 1959. Operation of the pilot plant was as follows: RT-12 grade road tar, pulverized Kentucky coal and high-boiling coal tar oil were transferred to a 1500 gallon digester from tank cars or tank trucks; the mixture was heated as rapidly as possible to 600 F, with agitation but without reflux, and maintained at that temperature for one half hour; by means of an internal water-cooling coil the temperature was reduced to 400 F and the finished binder was transferred to storage or transports. No major difficulties were encountered in the operation of the pilot plant in this manner.

During the construction of the pilot plant fifty four coal samples from eastern and western Kentucky coal mines were analyzed and tested on a miniature scale for digestibility in RT-12 at Quehanna. Three of the samples, selected as being representative of eastern and western Kentucky coals, were made into two and three component type binders (CW-II and CW-III). The latter were mixed in varying proportions with representative samples of Kentucky aggregates to establish the optimum binder content for Kentucky Class I hot-mixes in which they were to be used. By agreement with the Kentucky Highway Research Department a binder content of 7.0 percent was first used and later changed to 6.9 percent.

During the period between August 13th and November 7th 1959 one hundred and four batches of hot-mix binder, totalling approximately 150,000 gallons were made in the pilot plant. One hundred batches (144,000 gallons) were of the three component type (CW-III) with the following average composition, 81% RT-12, 11% high-boiling coal tar oil and 8% coal; two batches (3,000 gallons) of the two component

62. type (CW-II) contained 96% RT-12 and 4% coal, and two batches (3,000 gallons) contained only RT-12 which was heated to 400 F in the digester before delivery to test sites.

Kentucky Field Tests

The CW-III type binder was delivered to fourteen test sites in various parts of Kentucky. At twelve of the sites the binder was used in 1-1/2 inch Kentucky, Class I overlays on existing black top pavements which, for the most part, had required a large amount of maintenance because of base failures or the development of slippery-when-wet surfaces. At the other two test sites the CW-III binder was used in hot-mix that was laid 2-3/4 inches thick over tar-primed soil roads in accordance with Kentucky, Class I Modified Base specifications.

The CW-II type binder was used at only one location (8 miles south of London) in a 1-1/2 inch overlay of the Class I type.

The RT-12 road tar was used in a short 1-1/2 inch Class I overlay at the above location and also in a 2-3/4 inch, Class I, modified base near Bowling Green for comparison with the CW-III type of binder.

The hot mixes were made in eleven commercial, hot-mix plants of which six were batch and five continuous. No major difficulties were encountered at any of them in the use of the coal-modified binders. Also, except for somewhat excessive fuming when paving temperatures exceeded 260 F, paving operations by nine different contractors were very satisfactory even though atmospheric temperatures varied from about 27 F to 100 F during the construction period.

However, service results from the various test pavements were not entirely satisfactory. After the first winter, which was unusually severe, considerable surface abrasion, (due in part to tire chains), and cracking was observed particularly at center joints and near the edges where the new overlays projected beyond the original pavement surfaces. Cracking was particularly noticeable at locations where the 1-1/2 inch overlays were placed on old and unstable black top pavements that had required extensive maintenance in former years. It was obvious that the overlays containing the CW-III type binder (coal, RT-12 and high-boiling oil) were too hard and brittle and did not have enough flexibility, particularly at low temperatures, for use over unstable pavements.

At the one location (8 miles south of London) where overlays containing asphalt, RT-12, and each type of coal-modified tar binder (CW-II and CW-III) could be compared under identical conditions, it appeared that the one containing only RT-12 was least satisfactory because of excessive bleeding during summer months, the section containing CW-III binder (coal, RT-12 and oil) was too brittle and inflexible and the section containing the CW-II binder, (4% coal plus 96% RT-12) compared most favorably with the asphalt control section. It appeared to have more flexibility and less brittleness at low temperatures and a greater tendency to "self-heal" in hot weather, without bleeding excessively, than the CW-III binder made with 8% coal, 81% RT-12 and 11% oil.

Soon after the test sections were laid it was apparent that the coal-modified binders should have been somewhat softer, i.e., their initial ASTM penetrations at 25 C should have been higher, a somewhat greater proportion of each should have been used in the hot-mixes, and lower mixing and paving temperatures should have been used to minimize hardening due to the evaporation or sublimation of some of the tar oils. With a view to making further improvements, the Quehanna investigations were directed along the following lines during most of 1960.

By comparing the absolute viscosities, at different temperatures, of the four binders used in Kentucky it was concluded that mixing and paving temperatures in the range of 200 - 250 should be adequate for coal-modified binders of the CW-II and CW-III types.

Ten percent dispersions of coal in RT-12 were made with a large number of coal samples from various locations in North America, South America and Japan. Their softening points (R & B) varied from 40 C to 65 C but they all appeared to have approximately the same temperature susceptibilities in the range of 25 to 32 C. For these tests, 25 gram portions of each coal were dispersed in 225 grams of RT-12 by heating the mixture, with agitation and reflux of condensable vapors, to 600 F for one hour. The results were comparable to those obtained from Quehana autoclave and Kentucky pilot plant digestions.

Low, medium and high temperature coal tars distilled to RT-12 consistency were compared as dispersing media for Freeport seam coal. The distilled low temperature tar was unsatisfactory but dispersions made with RT-12 from two medium temperature tars compared favorably with a dispersion of the coal in RT-12 from high temperature coke oven tar.

Various polymers were added to a modified coal dispersion of the CW-III type (coal, RT-12, and oil). Included in these tests were Hycar latex, natural rubber latex, reclaimed rubber, Neoprene powder, Neoprene latex, Butyl rubber, Vistanex and Thiokol LP-3. Most of the mixtures sludged or crusted on heating at 325 F for five hours. Vistanex, Butyl rubber and Thiokol were best in this respect and appeared to effect some improvement in the temperature susceptibilities of the coal modified tars.

Three aromatic oils of petroleum origin were tried, in place of high boiling coal tar oil, as plasticizers or fluxes but were incompatible when the mixtures were heated.

Promising results were obtained by adding high-penetration, petroleum residuals (180 - 200 or 250 - 300) to a dispersion of coal in RT-12. Temperature susceptibilities, particularly in the range below 25 C appeared to be substantially improved.

A sand blast method of test described by Rhodes and Gillander in 1936¹¹ appeared to be especially suitable for measuring the brittleness of hot mix binders particularly at low temperatures.

Bureau of Public Roads Investigations

As previously stated, the U.S. Bureau of Public Roads made independent studies of the asphalt, RT-12 and coal-modified tar binders used in the Kentucky experiments. They found that the temperature susceptibility of the CW-III binder was slightly lower than that of the RT-12 but not as low as the temperature susceptibility of the Kentucky 85-100 penetration asphalt cement; the absolute viscosities of the coal-modified tar binders were intermediate between those of the RT-12 and the asphalt cement; when subjected to thin-film oven tests the losses from CW-III were somewhat lower and retained-penetrations were somewhat higher than those of RT-12 but asphalt cement was better than either in both respects; oven ageing at 140 F for 30 days caused the Marshall stabilities of briquets made with the different binders to increase as follows, RT-12 439 pounds, CW-III 2248 pounds, asphalt cement 336 pounds; development of structure or reversible hardening took place to the greatest extent in the coal modified binder (CW-III), to a lesser extent in the

64. asphalt cement and, apparently not at all in the RT-12 when thin films of each were sealed between glass plates and heated at 110 F for 13 days; immersion of quartzite briquets in water at 120 F for 18 days caused those containing CW-III to lose 8% in strength and to swell 0.2% whereas decrease in strength for asphalt briquets was 44% and swell amounted to 1.4%; unconfined compression tests indicated that the coal modified tar binder should provide higher stabilities than the asphalt cement at any temperatures encountered in service. At 0° F the stabilities of specimens containing RT-12 and CW-III were about double the stability of the asphalt specimens and were in the range of strength of Portland cement concrete. In general the Bureau of Public Roads report concluded that coal-modified tar binders, such as those made by Curtiss-Wright, should be considered as improved tars that would be expected to perform better than unmodified tars in a number of applications but normal precautions should be employed when using them rather than attempting to substitute them for penetration grade asphalts.

Conclusion

Although major efforts have been made in Great Britain, South Africa and the United States to use coal-in-tar dispersions as highway construction materials, commercial success has not yet been achieved. A large amount of important information has been contributed by the investigations conducted to date but additional work is needed particularly along the following lines.

Methods for determining the temperature susceptibilities and, particularly, the brittleness at low temperatures of bituminous, hot-mix binders that have been used by previous investigators in this field should be compared and, if necessary, a new method should be developed. A few tests by Curtiss-Wright indicated that a sand-blast method might be especially suitable and additional tests should be performed. Also better methods for evaluating and comparing hot-mixes containing asphalt and coal-modified binders should be selected or developed in order, by means of laboratory tests, to predict most accurately the service lives of the finished pavements.

Formulations for road binders of the coal-dispersion types should be further improved. Most needed in this connection are better and less expensive plasticizers for use in place of high-boiling coal tar oil. Some of the materials which should be considered in this connection are water-gas and oil-gas tars and distillates therefrom, low-temperature and mid-temperature tars and tar oils and also petroleum distillates, extracts and residues. High boiling oil from heavy water gas tar is known to have good possibilities in this connection and tests made by Karius and Dickinson and also by Curtiss-Wright indicated that soft (high-penetration) asphalts should be especially interesting.

Continuous, rather than batch digestion of coal should be tried. Heretofore batch methods have been used exclusively for the commercial, pilot plant and laboratory dispersion of coal-as-coal in tars and tar oils. However, finely pulverized coal dissolves so rapidly and completely that continuous digestion with inexpensive equipment should be practicable.

Also the use of coal modified binders in highway subgrades and bases as well as surface courses should be tried. Because of the high strengths of mixes containing them and because of their extreme resistance to destruction by water, superior adhesion to aggregates and ability to penetrate soils and damp or dusty aggregates, coal dispersions made with coal tars and tar oils should be especially suitable for subgrade and base stabilization whereas coal-in-tar dispersions containing materials such as high penetration asphalts might be more suitable for use in surface courses.

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EFFECT OF AGGREGATE ON COKING OF BINDER IN PETROLEUM COKE-PITCH MIXTURES

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During investigation of pitches, it was observed that when pitch and calcined petroleum coke were mixed together and heated at about 150°C, the paste showed striking differences; its appearance varied from wet and sticky to sandy and dry, as proportions of the two components were changed. The transition was sharp, and the binder:aggregate ratio at which it occurred varied for a number of pitches, in some cases even for pitches of similar softening points. It was also found that increasing the temperature intensified the interaction between pitch and aggregate and enhanced differences in appearance of the heated mixtures. These qualitative observations were followed by quantitative tests involving preheating steps at temperatures below 400°C followed by a coking treatment at 550°C. Several mixtures were prepared containing from 30 to 70% of -200 mesh calcined petroleum coke in increments of 3 to 10%. After thorough mixing, the mixtures were placed in porcelain crucibles fitted with a lid and the whole was imbedded in calcined petroleum coke inside a nickel crucible. After heating for 30 minutes at 200°C and 30 minutes at 300°C in a muffle furnace, the mixtures were coked at 550°C for two hours. The percentage of original pitch converted into coke was calculated from the total carbon residue corrected for the original weight of aggregate; weight loss of the aggregate itself was negligible.

FIGURE 1, illustrates the effect of preheating on the amount of pitch coke formed during the coking step. With no preheating, the yield of pitch coke remains fairly constant over the entire range of binder:aggregate ratios, and is substantially the same as the coking value of the pitch determined separately. With the mixtures preheated at 200 and 300°C, the results are quite different. For high contents, variations in pitch coke yield are not significant. However, when the pitch content decreases to a point - which we call the "saturation point" - where the mixture presumably is no longer saturated with pitch, the pitch coke yield increases suddenly up to a level at which it remains fairly constant even with further reduction in pitch content. The sharp increase in pitch coke yield coincides with the visible change in the appearance of mixtures mentioned previously.

The shape of the curve and location of the saturation point are influenced by the particle size of the aggregate as shown in FIGURE 2. The heating programme was also found to be critical, especially in the range from 200 to 400°C where the pitch is extremely mobile and shows high wetting power towards the aggregate.

The increase in amount of pitch coke formed might be attributed to the retention of increasing quantities of volatile pitch fractions as the aggregate proportion in the mix increases; however, this increase in pitch coke yield would be expected to be gradual and not as sudden as the actually observed change. On the other hand, increasing the aggregate particle size results in a flattening of the curve indicating that surface area is also a factor. This is further supported by our findings that the increased coke yield occurs only with surface-active materials such as Fuller's earth and molecular sieves, whereas it does not so with a material such as glass powder which exhibits no surface activity. Surface area alone cannot, however, offer a complete explanation. The fact that the sharp increase can be obtained only

after pitch: aggregate mixtures have been given a preheating treatment should also be taken into consideration. Preheating probably permits pitch to displace the air or other gases absorbed by the aggregate and to enter into better contact with the latter before being coked. When coking is carried out without preheating, any gases escaping from the aggregate surface presumably interfere with the interaction between the two components. Other factors are undoubtedly involved and consequently no full explanation can yet be offered for the increase in pitch coke yield when binder and petroleum coke are mixed and heated under controlled conditions.

The technique described above provides an additional test for comparison of binders from different sources or of different types; TABLE 1 lists some results obtained and shows that saturation point tends to vary with quinoline insoluble content, but cannot be related to softening point or coking value. The procedure can also be applied to comparison of aggregate cokes, and in certain cases to estimation of binder requirements.

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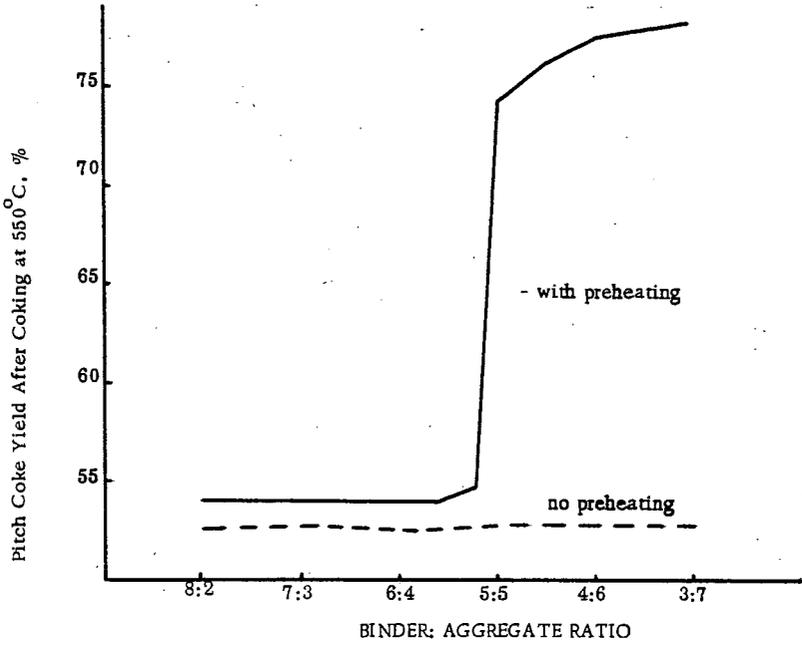


FIGURE 1

EFFECT OF PREHEATING ON PITCH COKE YIELD IN BINDER: AGGREGATE MIXTURE

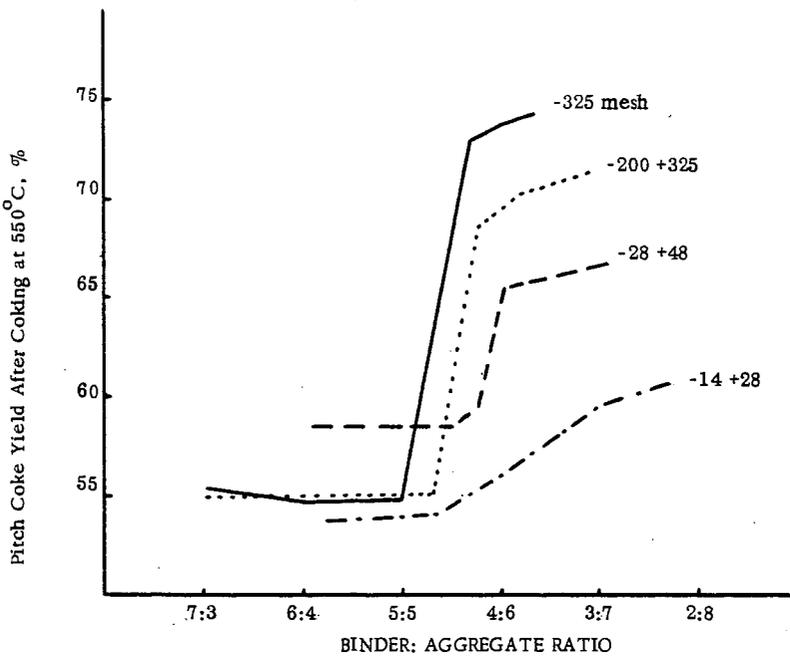


FIGURE 2

EFFECT OF PARTICLE SIZE OF AGGREGATE ON SATURATION POINT AND CURVE

TABLE 1
SATURATION POINTS OF PITCHES FROM VARIOUS SOURCES

Source ^(a)	Pitch ^(b) Type	% Pitch at Saturation Point	Softening Point Cube-in-Air, °C	Coking ^(c) Value %	Quinoline Insoluble %
A	CTP	75	100	62	29
		69	137	65	24
		57	111	62	14
		57	99	55	12
		53	102	53	4
B	CTP	57	50	45	13
		54	115	58	5
		53	112	55	5
		53	87	52	8
C	CTP	57	109	58	11
		53	107	56	8
D	CTP	59	109	57	11
E	CTP	57	92	57	13
F	PP	54	109	54	3
		49	114	56	2
G	PP	50	115	54	0

(a) Letters represent different pitch producers.

(b) CTP = coal-tar pitch
PP = petroleum-base pitch

(c) By regular coking value method. Ref. Fuel, XXXVII, 382-392 (1958)

Pipeline Gas from Oil Shale by Direct Hydrogasification

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INTRODUCTION

The gas industry has been studying methods for the production of natural gas substitutes from coal and petroleum oils. Processes for direct conversion of these fossil fuels to high heating value gases consisting largely of methane are in an advanced stage of development (6,7). In the case of oil shale, existing technology would involve a preliminary retorting step to produce crude shale oil, and refining to prepare a suitable feed for continuous destructive hydrogenation (hydrogasification). It was reasoned that a direct oil shale hydrogasification process might be preferable because of potentially higher conversion of the organic matter to gas, and elimination of a number of process steps.

Feasibility was shown for direct hydrogasification of the organic matter in Green River oil shale. High heating value gases were produced (1,9,13) in batch reactor tests at 1300°F. at 1200 to 5500 p.s.i.g., and with 100% of the stoichiometric hydrogen requirement for complete conversion of the organic matter to methane. About 90% or more of the organic carbon plus hydrogen content of the oil shale was converted to methane and ethane.

In these tests, the path of the hydrogenolysis of kerogen was only partially indicated at the long heatup times and long gas residence times encountered in the batch reactor. Only the slower final breakdown of higher gaseous paraffins to methane and ethane could be observed. It was also not possible to measure overall reaction rates and precisely determine the effects of temperature. Pressure effects were obscured by changes with temperature and degree of conversion.

The present work was conducted in a reactor system in which oil shale heatup times and exit gas holdup times in the heated portion of the reactor were of the order of a few seconds. After leaving the reactor, the reaction products were cooled rapidly to minimize further reactions.

Three separate test series were conducted. The first test series consisted of semiflow tests with short gas residence times. The purpose of these tests was to measure the rate of kerogen conversion to gaseous products and the rate of mineral carbonate decomposition. The second test series was conducted with a bed of inerts downstream of the oil shale charge, to simulate hot-spent oil shale in a cocurrent flow reactor and to provide time for secondary vapor-phase hydrogenolysis reactions. Here, the overall space velocity which gave methane and ethane as the major products was determined. The third test series consisted of simulated continuous feeding tests to measure the average instantaneous rates of production of gaseous hydrocarbons at controlled hydrogen-to-oil-shale feed ratios.

EXPERIMENTAL

Apparatus

A schematic diagram of the semiflow reactor system is shown in Figure 1. The reactor contained a self-sealing, modified Bridgman closure at each end and was 2 inches in inside diameter, 4 inches in outside diameter, and 60 inches in inside length. The reactor barrel, constructed of Uniloy N-155 super alloy, was rated for operation at a maximum temperature of 1700°F. at 1500 p.s.i.g. The closures were

rated for a maximum temperature of 1400°F. at 1500 p.s.i.g. Satisfactory closure operation was obtained with both 16-25-6 and Inconel-X seal rings. A boundary lubricant of molybdenum disulfide, applied in aerosol form, was used on all closure threads and on the seal rings to prevent galling. This reactor has been completely described elsewhere(11) along with design details which describe the use of externally heated reactors at combined high temperatures and high pressures.

An Inconel-X thermowell of 3/8-inch outside diameter, with a 12-gage wall thickness and 58 inches long, was mounted axially in the bottom closure. The thermowell could contain up to five 0.040-inch outside diameter thermocouples. Thermocouples were chromel-alumel, magnesium oxide insulated, and enclosed in a swaged Inconel sheath. To provide for complete containment and recovery of the oil shale residue, the reactor was provided with a removable stainless steel insert, 1-5/8 inches in inside diameter by 1.990 inches in outside diameter and containing a 1/2-inch outside diameter thermowell sleeve.

The reactor was heated by means of an electric resistance furnace containing four separately controlled heating zones, consisting of four rectangular heating elements, 7 inches wide and 12 inches long. Temperatures were controlled manually during tests but were controlled by pyrometric controllers during reactor heatup. Each temperature was recorded at approximately 3-second intervals by means of a high-speed potentiometric temperature recorder during the test period.

A feed hopper was mounted directly above the reactor and was provided with a vibrator to aid oil shale feeding. A full-opening, air-operated ball valve was installed between the hopper and the reactor. A second hopper contained a rotating-drum type feeder, which was driven by a variable speed drive, for continuous oil shale feeding.

Feed hydrogen flow rates were controlled manually and were measured by means of an orifice meter. The orifice pressure and the reactor pressure were recorded continuously. The feed hydrogen was preheated to reaction temperature within the reactor. Exit gases passed through a water-cooled coil, a liquids knockout pot, a high-pressure filter and a pressure-reducing back-pressure regulator, before being sampled, metered and monitored. A sampling manifold was installed upstream of the metering and monitoring system. The exit gas specific gravity was monitored by means of a recording gravitometer.

Materials

In all tests, the feed hydrogen contained an accurately measured small amount of helium, usually 1-2 mole %, as a tracer for exit gas flow rate measurement. The gases were mixed during compression and stored in high-pressure cylinders at pressures up to 3000 p.s.i.g. Commercially available grades of electrolytic hydrogen (99.8% pure) and helium (99.99% pure) were used. The oil shale used in all semiflow tests was supplied by the Union Oil Company. An analysis of the oil shale is given in Table I.

Procedure

The semiflow experimental technique employed in the majority of the tests followed closely that employed in coal hydrogenolysis studies described recently (2,11). Most tests were of 15-minute duration or less. After the reactor was heated to the desired operating temperature, the unit was pressurized and gas flow was

started. Heat inputs were then adjusted until all recorded reactor temperatures remained constant. When flow rates, temperatures, and pressures had been stabilized completely, the feed gas was sampled. Tests were initiated by opening the quick-opening ball valve connecting the hopper and the reactor. The vibrator mounted on the hopper was started only a few seconds before the start of the run to avoid compacting the oil shale charge.

The feed gas orifice calibration was checked before each run with a wet test meter. Exit gases were also metered with the wet test meter during each test, as a check on the flow rates calculated using the helium tracer. The exit gas specific gravity record was used as an aid in selecting times for exit gas sampling; in tests conducted to simulate continuous operation, it was also used to check the length of the oil shale feeding period, since it was not always possible to obtain positive proof of the initiation of solids feeding. Gas analyses were performed by mass spectrometer. Except for the last three tests conducted in the series to simulate continuous operation, combined values for nitrogen plus carbon monoxide are reported, because of the inability to distinguish precisely between these two gases by the mass spectrometer. In the last three tests, carbon monoxide was also determined by infrared spectrophotometer and nitrogen was obtained by difference.

In the first series of tests, single charges of oil shale weighing from 10 to 200 grams were fed. These charges were allowed to fall freely from the hopper, which resulted in a charging rate of about 7 grams per second. Small amounts of high-purity alumina inerts, up to 4 inches in depth, were placed in the reactor before the run to support the shale charge and to position it in the center of the third reactor heating zone. Temperatures were recorded for thermocouples located at the center of the oil shale charge and at a point 6 inches above the charge to show whether the feed hydrogen was being preheated completely before reaching the charge.

Table I.-ANALYSIS OF COLORADO OIL SHALE

Sample Designation	4770
Type	Colorado, Mahogany Zone
Source	Union Oil Company
Particle Size, U.S. Standard Sieve	-8,+20
Analysis, wt. % (dry basis)	
Moisture	0.3 ^d
Organic Carbon ^a	17.45
Mineral Carbon ^b	4.84
Hydrogen ^a	2.36
Organic C/H Wt. Ratio	7.4
Fischer Assay Oil, gal./ton ^c dry shale	35.9

- ASTM method D271-58 adapted in accordance with technique of Grace and Gauger (3).
- Method A-3, U. S. Bureau of Mines.
- Modified method of Stanfield and Frost (14).
- On oven-dry basis (dried for 1 hr. at 105°-110°C.).

Since the void volume in the bed of inerts was small, exit gas holdup times in the system downstream of the reaction zone were small. At typical operating conditions of 1300°F., 1000 p.s.i.g., and 100 SCF per hr. feed hydrogen flow rate, the total exit gas holdup time was only about 10 seconds, based on the appearance of the first hydrogasification products in the exit gas sample. Gas residence times in the reactor proper at these conditions were less than 5 seconds. During the initial period of high rate of hydrogasification, gas samples were taken at intervals as short as 5 seconds and thereafter at time intervals sufficiently small to delineate the entire course of the reaction. The last gas sample was usually taken at 480 seconds, at which time its methane content was less than 0.1 mole %.

The second series of tests was conducted with larger amounts of alumina inerts below the oil shale bed to provide sufficient residence time for the primary reaction products to undergo further hydrogasification after leaving the reaction zone. Sufficient alumina inerts, to simulate spent shale, were placed in the reactor prior to each test to give a total bed volume (oil shale plus inerts) of 0.02 cu. ft. Since gas flow rates were varied from 10 to 200 SCF per hr., the feed hydrogen space velocity varied from 500 to 10,000 SCF per cu. ft. bed-hr., and exit gas holdup times ranged from about 200 to about 10 seconds, respectively. Temperatures of the center of the inerts and of the bottom of the oil shale charge were recorded. Here, as in earlier tests, gas samples were taken at those time intervals required to delineate the entire course of the reaction.

In the third series of tests, continuous operation was simulated by semicontinuous feeding of oil shale. In the first few tests, oil shale was fed by opening the ball valve, connecting the reactor and feed hopper, every 15 or 20 seconds for 1 second and for total charging times of from 465 to 840 seconds. In later tests, conducted with a rotating drum-type feeder, oil shale feed rates were about 5.5 pounds per hour. Approximately 0.01 cu. ft. of alumina inerts was placed in the reactor prior to each of these tests to minimize changes in feed hydrogen space velocity accompanying bed volume changes, and to provide a zone simulating a bed of spent oil shale wherein primary reaction products could be further reacted. This resulted in a total bed volume (oil shale plus inerts) which increased to a final value averaging about 0.02 cu. ft. Since, in these tests, the inlet hydrogen-to-oil-shale ratio was varied by varying gas flow rates, the exit gas holdup times also varied. Temperatures of the bottom of the oil shale bed, of the bottom of the inerts, and of the center of the final oil shale bed were recorded. Gas samples were taken during and after the feeding period.

Exploratory Tests

Exploratory tests to select the proper combinations of oil shale sample weights and feed hydrogen flow rates were made at 1300°F. and 1000 p.s.i.g.

To approach isothermal as well as differential reactor conditions, it was necessary that the smallest oil shale sample weights be used for a given feed gas flow rate which still permitted accurate product analysis. However, it was also necessary to maintain a sufficient sample size so that representative samples of the highly heterogeneous feed could be prepared by riffing of larger batches.

Feed gas flow rates were set as high as possible to keep the residence time of the reaction products in the exit gas system small so as to minimize secondary vapor phase reactions. This also minimized backmixing of reaction products in the exit gas system and oil shale particle heatup times. A feed hydrogen flow rate of 100 SCF per hour was calculated to be the minimum gas flow rate which could be used, assuming complete mixing in the exit gas system, without distorting the true relationship between reaction rate and time.

With 50- and 25-gram samples, the maximum exit gas hydrocarbon concentration was too high at this hydrogen feed rate, and temperatures changed too greatly to allow the assumption of differential and isothermal reaction conditions. In tests with 10-gram samples, exit gas hydrocarbon concentrations and reaction zone temperature changes approached practical limiting values. With such small samples, however, quantitative recovery of liquids was not possible.

The observed rates of conversion may have been largely a function of heat transfer. The lack of accurate thermophysical data for oil shales makes calculation of particle temperatures difficult. However, heat transfer calculations indicated that the -8, +20 U.S.S. size oil shale particles would be preheated to at least 1100°F. in falling from the hopper through the top two reactor heating zones.

As shown in Figure 2, there were large increases in the specific rate of conversion, expressed as pounds of carbon as gaseous aliphatic hydrocarbons formed per pound of organic carbon fed per hour, with decreases in sample weight. Therefore, to obtain differential rates of reaction, it was necessary to prepare a cross-plot of reaction rates versus sample weight at selected levels of organic carbon conversion. By plotting on semilogarithmic coordinates (logarithm of reaction rate versus sample weight) a family of curves was obtained for the parameter, percent conversion. These curves approached straight lines as sample weights approached zero so that reasonably good rate values for zero sample weight could be obtained by linear extrapolation. Reaction rates obtained by this cross-plotting technique are shown in Figure 3, as a function of conversion.

RESULTS

Single-Charge Tests at Short Gaseous Product Residence Times

A series of tests was conducted at temperatures of 1100°, 1200°, 1300° and 1400°F. to measure the effect of temperature and conversion on gaseous aliphatic hydrocarbons on the rate of conversion of organic carbon (Figure 4). These results show a large increase in rate with increases in temperature. The effects of increases in temperature and hydrogen flow rate on gaseous and total product distribution are shown in Figures 5 and 6. The gaseous aliphatic hydrocarbon yields, and the percentage of paraffins, increased with increases in temperature and decreased with increases in feed hydrogen flow rate. The variation of liquid yields was the opposite of gas yields. These results indicate that the major steps in the hydrogenolysis of kerogen are:

- 1) Kerogen decomposition with initial formation of intermediates at least partially recoverable as liquids at very short residence times and/or low temperatures.

- 2) Pyrolysis, hydrogenation and hydrogenolysis reactions leading to gaseous aliphatic hydrocarbons of decreasing molecular weight and, finally, ethane and methane, along with some aromatic liquids.

A comparison of the gaseous molecular hydrogen consumption with the elemental gaseous hydrogen balance is given in Figure 7. At low levels of organic carbon conversion to gaseous aliphatic hydrocarbons, the amount of hydrogen donated by the oil shale is approximately equal to the amount of feed hydrogen consumed. Thus, pyrolysis and hydrogenation reactions probably occur simultaneously. At high conversion levels, no accurate measurement can be made.

Rates of carbonate decomposition were also measured, although separate infrared spectrophotometer analyses were not performed for carbon monoxide. Mass spectrometer analyses indicated, however, that nitrogen was negligible in comparison to carbon oxides. The strong increase in decomposition rate with increase in temperature is shown graphically in Figure 8. These rates are much higher than those measured by Jukkola and others (4) in nitrogen or carbon dioxide at 1 atmosphere. This may be due to the more rapid oil shale heatup and the lower concentration of carbon dioxide in these tests. The large increase in decomposition rate between 1200°F. and 1300°F. is probably due to the combined decomposition of both magnesium carbonate and calcium carbonate above 1200°F. Jukkola and others (4) found that calcite in oil shale begins to dissociate at 1150° to 1250°F. Since the molar ratio of calcium carbonate to magnesium carbonate is 2.3 in this oil shale any rate differences in a transition from a region where only magnesium carbonate decomposes at a measurable rate to one where both carbonates decompose measurably fast would be accentuated. It would be desirable to minimize mineral carbonate decomposition in large-scale processing since the decomposition reactions are endothermic and part of the feed hydrogen is consumed by reaction with part of the carbon dioxide formed. Equilibrium carbon dioxide partial pressures for magnesium and calcium carbonate breakdown, shown in Figure 9, indicate that it might be feasible to inhibit calcium carbonate decomposition, but not magnesium carbonate decomposition, by maintaining a high carbon dioxide partial pressure.

Single-Charge Tests at Long Product Residence Times

There were several shortcomings in the above tests. First, product residence times were short and liquid and olefinic gaseous hydrocarbons were major products. Second, product residence times in the reactor could not be practically controlled since they were a function of many other variables (e.g., temperature, pressure, flow rate and oil shale sample size). For process design purposes, it is necessary to show the effects of variables under conditions where gaseous paraffins are the primary products.

Therefore, the test program was supplemented by tests using a bed of inerts downstream from the oil shale bed to simulate spent oil shale in a practical reactor system, which would allow further conversion of higher molecular weight hydrocarbons to gaseous paraffins. As can be seen in Figure 10, the above objective was met in these tests. The fraction of gaseous hydrocarbon carbon appearing as methane plus ethane was about 80 % or more over the entire range of space velocities employed. In addition, only about 2% or less of the gaseous hydrocarbon carbon was nonparaffinic.

The results shown in Figure 10 are consistent with the reaction sequence described earlier. At the lower feed hydrogen space velocities, the conversion to gaseous hydrocarbons was reduced by coke formation due to the lack of sufficient hydrogen. At the higher feed hydrogen space velocities, the conversion to gaseous hydrocarbons reached a nearly constant value. The slight decrease at the highest feed hydrogen space velocities was accompanied by an increase in liquids, which indicates that products residence times were insufficient for conversion of liquid intermediates to gaseous hydrocarbons. The apparent increase in the maximum rate of conversion to gaseous hydrocarbons with increases in feed hydrogen space velocity above 5000 SCF/cu. ft.-hr. was primarily the result of increased linear velocity of the rapidly formed intermediate reaction products. Backmixing effects were found to be negligible over most of the range of flow rates studied (5).

Simulated Continuous Tests

In view of the important effect of the hydrogen-to-oil-shale feed ratio on product distribution, the semiflow techniques were modified to permit control of this variable. Initially, small batches of oil shale were fed at frequent intervals onto a fixed bed of inerts. Results still showed an apparent effect of feed ratio above 100% of the stoichiometric requirements for conversion of the organic matter to methane, which was unexpected on the basis of oil hydrogasification results (8,10,12). However, these tests showed the expected negligible effect of an increase in total pressure from 1000 to 2000 p.s.i.g.

Further tests at 1200° to 1400°F. and 1000 p.s.i.g. were then conducted with a continuous feeding system in which oil shale was charged at a nearly constant rate for 510 seconds, corresponding to an average oil shale residence time of about 5 minutes. Thus, the hydrogen flow rate increased linearly with hydrogen-to-oil-shale ratio. As shown in Figure 11, instantaneous organic carbon gasification at hydrogen-to-oil-shale feed ratios ranging from about 100 to 250% of stoichiometric remained nearly constant and averaged 63 to 64%. Total organic carbon gasification measured during the 1000-1100 second run period was about 70%. The organic carbon distribution in the residue and the aromatic liquid products was about 13% each, at the lowest gas rate. The organic carbon in the residue decreased with an increase in hydrogen feed rate, as would be expected. All yield and organic carbon distribution data are uncorrected for low carbon balances (92 to 96%).

Higher conversions to gaseous hydrocarbons could, of course, be obtained by increasing oil shale residence times, although the maximum would be about 85 to 90% since a minimum yield of aromatic liquids of 10 to 15% would be expected from previous experience in hydrogasification of petroleum hydrocarbons similar in composition to kerosene (8,10,12).

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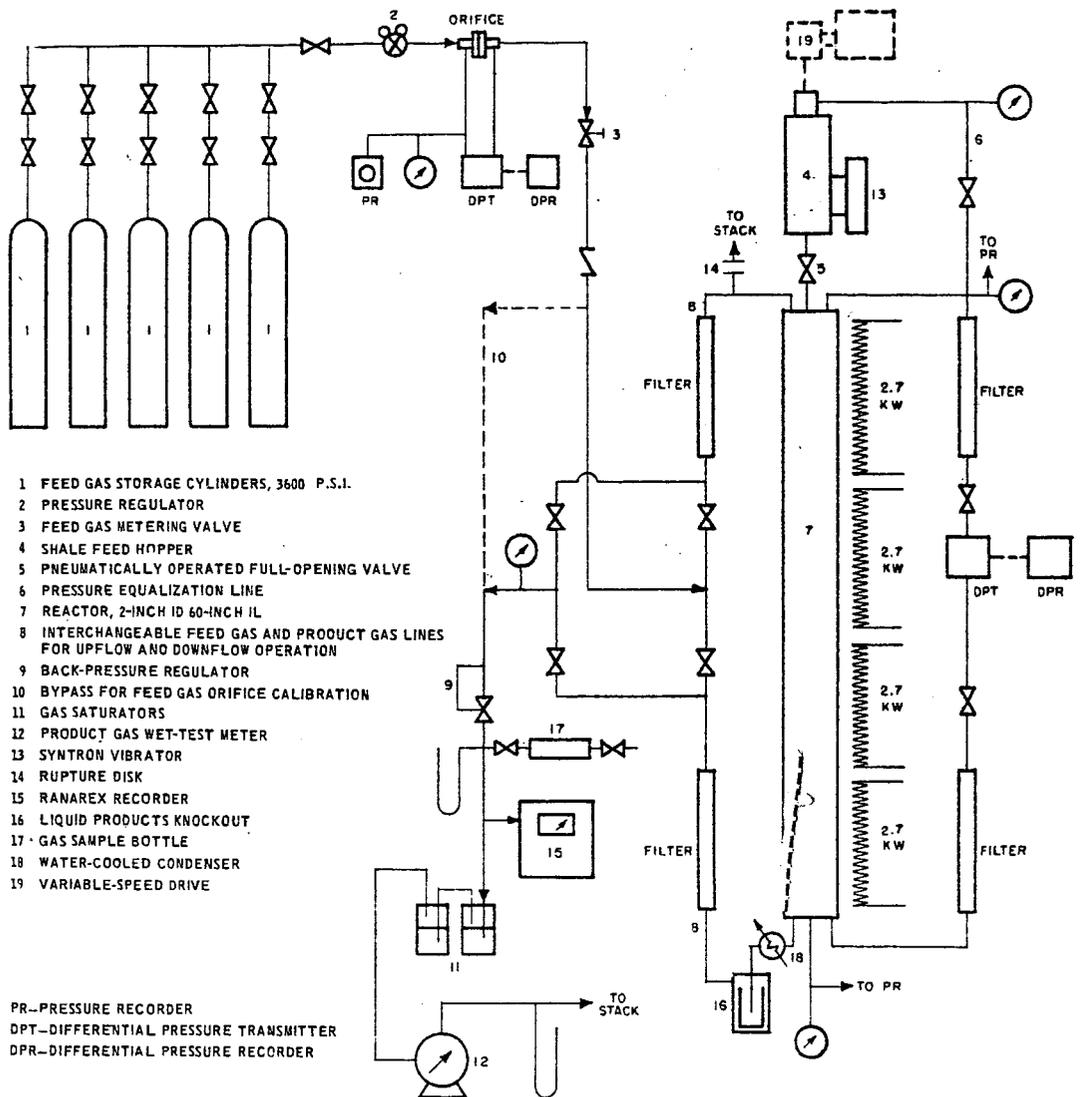


Fig. 1. Semiflow Reactor System for Study of Rates of Hydrogasification of Oil Shale at Temperatures to 1700° F and Pressures to 3000 p.s.i.g.

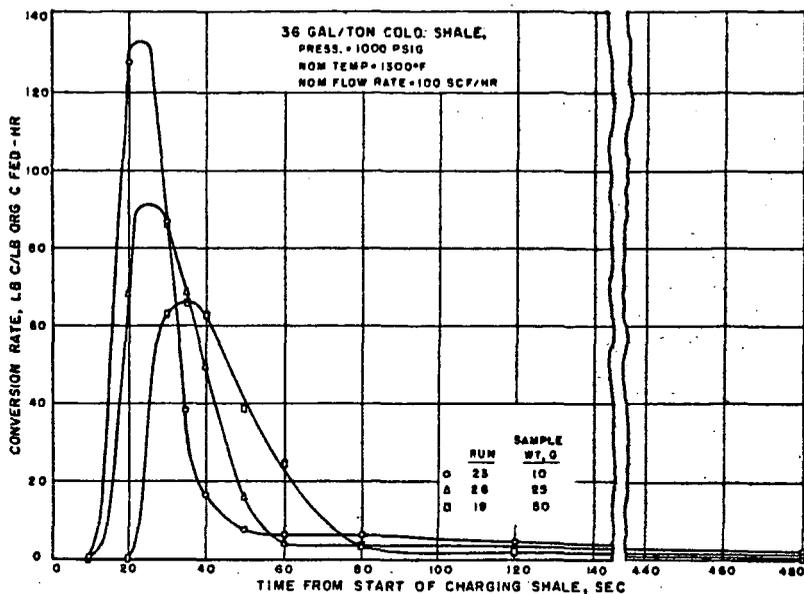


Fig. 2.-Effects of Sample Weight and Time on Rate of Conversion of Organic Carbon in Oil Shale to Gaseous Aliphatic Hydrocarbons

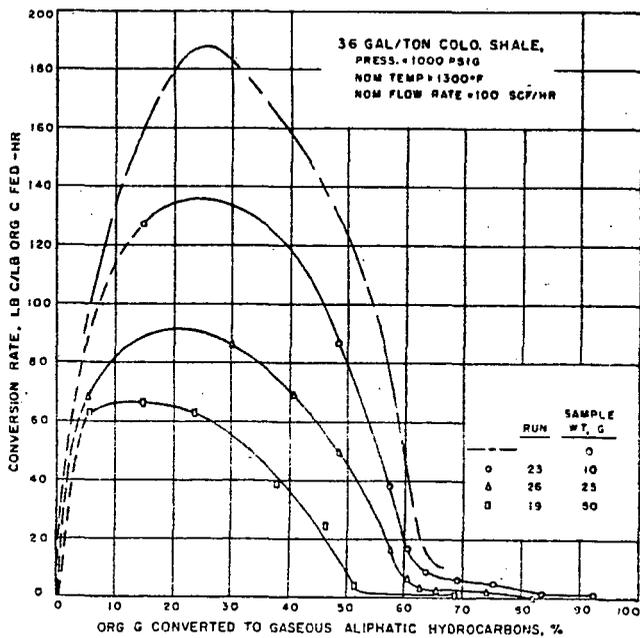


Fig. 3.-Effects of Oil Shale Sample Weight and Organic Carbon Converted to Gaseous Aliphatic Hydrocarbons on Conversion Rate

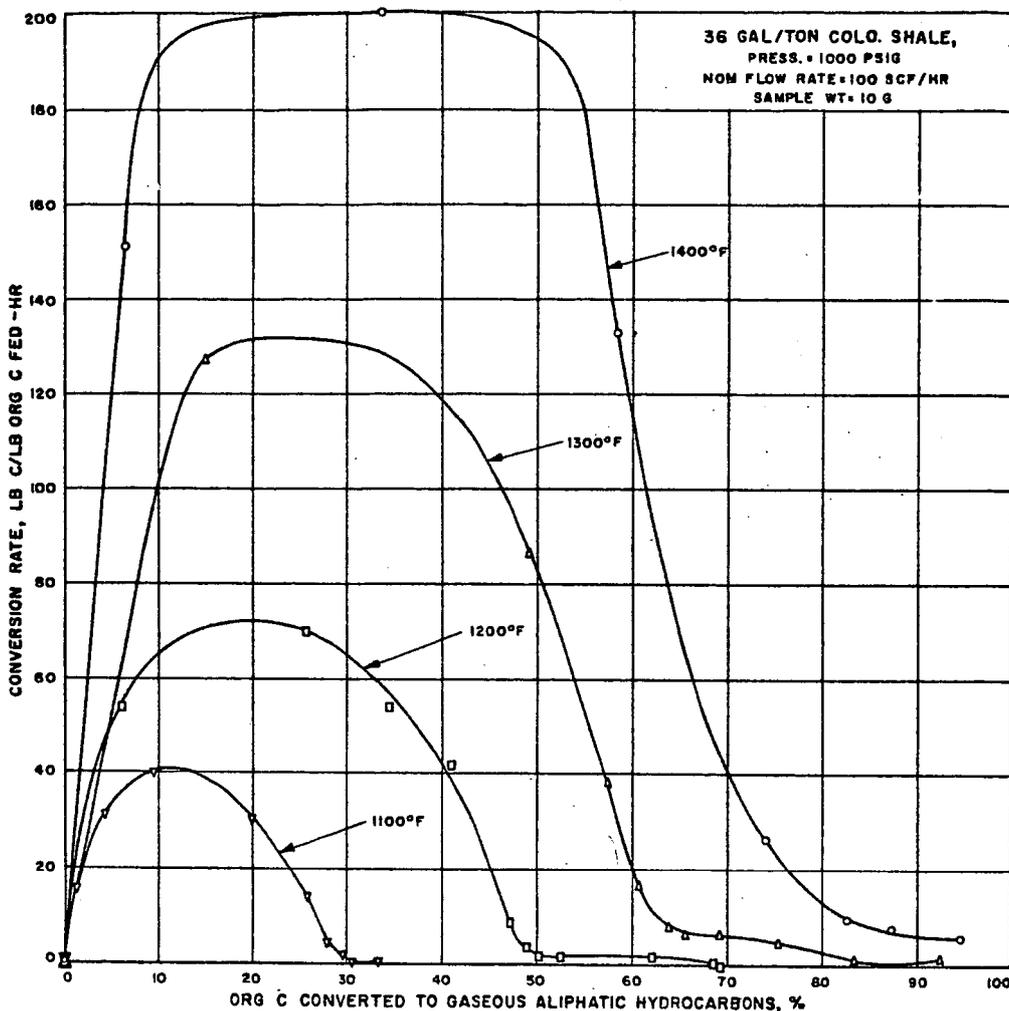


Fig. 4.-Effects of Temperature and Organic Carbon Conversion to Gaseous Aliphatic Hydrocarbons on Conversion Rate

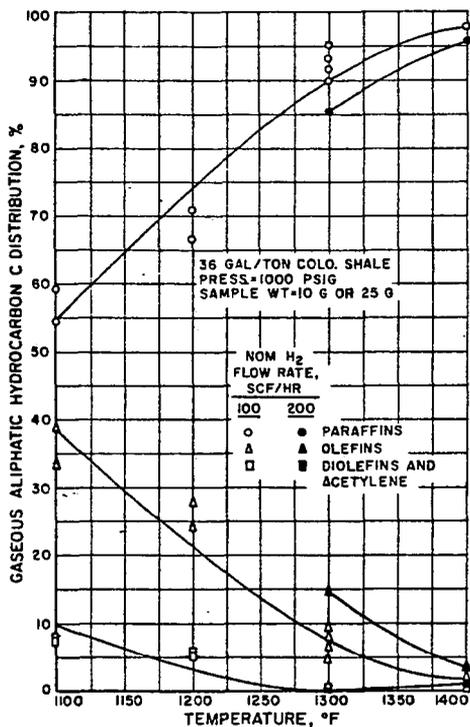


Fig. 5.-Effects of Temperature and Feed Hydrogen Flow Rate on Average Gaseous Aliphatic Hydrocarbon Distribution During First Minute of Gasification

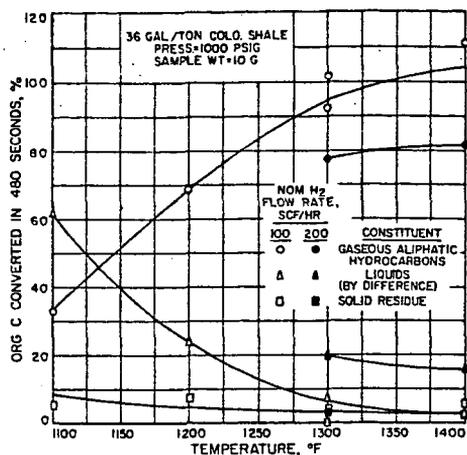


Fig. 6.-Effects of Temperature and Feed Hydrogen Flow Rate on Conversion of Organic Carbon to Gaseous Aliphatic Hydrocarbons, Liquids and Solid Residue

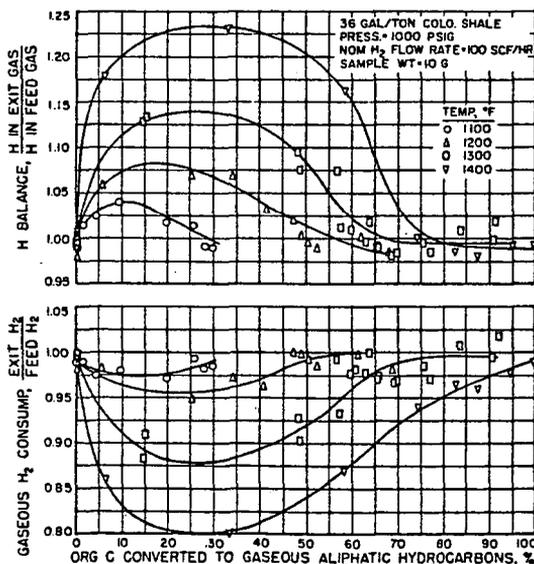


Fig. 7.-Gaseous Hydrogen Balances as a Function of Temperature and Organic Carbon Conversion

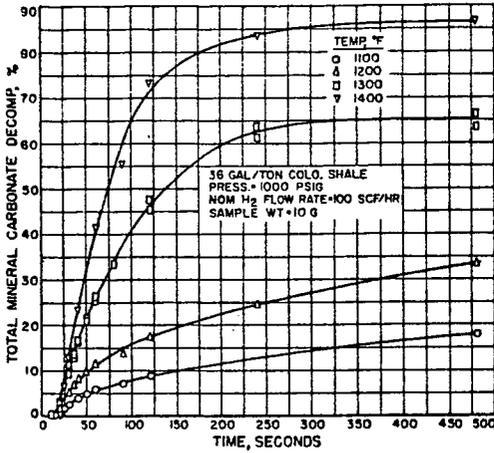


Fig. 8.-Effects of Temperature and Time on Mineral Carbonate Decomposition

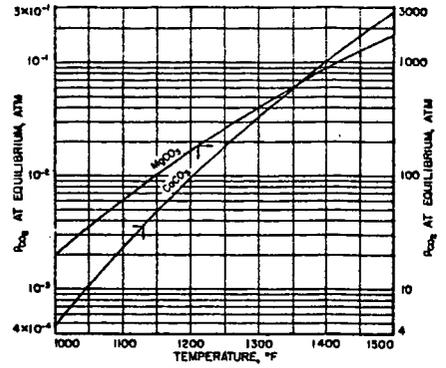


Fig. 9.-Effect of Temperature on Equilibrium Carbon Dioxide Partial Pressures for Magnesium Carbonate and Calcium Carbonate Decomposition

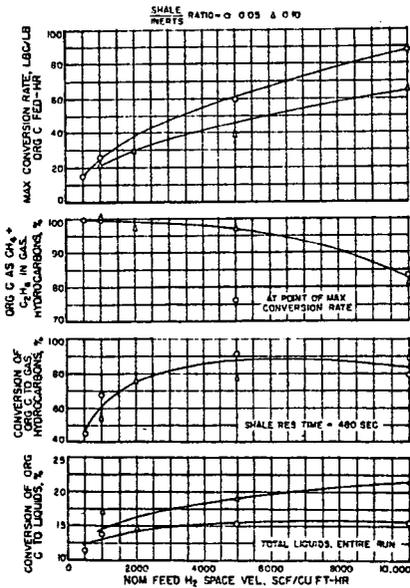


Fig. 10.-Effect of Feed Hydrogen Space Velocity on Organic Carbon Converted to Liquids and Ethane Plus Methane and on the Maximum Conversion Rate

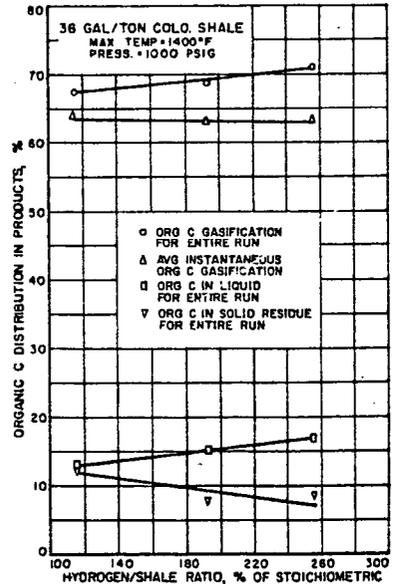


Fig. 11.-Effect of Hydrogen/Shale Ratio on Carbon Distribution in Products and Average Instantaneous Carbon Gasification