approximately 40 times as rapidly as trimethyl trimellitate and, hence, the distillate from an equi-molecular mixture will be much richer in the more volatile component.

In Fig. 3 are shown plots of an exhaustive stepwise distillation of an approximately equi-molecular mix of the neutral methyl esters of *o*-phthalic, trimellitic, pyromellitic, benzene pentacarboxylic and mellitic acids. The solid line shows the cumulative per cent. distillate as a function of time and the triangles the methoxyl content of the fractions. It is evident that by such a procedure a rough fractionation is effected and that by the application of this process to an unknown mixture of methyl esters of the benzene carboxylic series information can be obtained, on even small samples, of the relative amounts of the various members of the series present. The application of this method of examination to the mixture of esters of the acids obtained by alkaline permanganate oxidation of bituminous coal will be described elsewhere.

Summary

Rates of distillation in vacuum of the methyl esters of *o*-phthalic, trimesic, trimellitic, hemimellitic, prehnitic, mellophanic, pyromellitic, benzene pentacarboxylic and mellitic acids have been measured. Plots of the log of the rate against the reciprocal of the absolute temperature are linear. The slopes of these lines lead to values of heats of vaporization ranging from 13 kcal. for dimethyl *o*-phthalate to 29 kcal. for hexamethyl mellitate. No significant difference was found in the rates of distillation of the methyl esters of isomeric acids except with the tetracarboxylic acids where there was evidence that the pyromellitic is the most volatile. The rate of distillation of trimethyl trimellitate was found to be of the same order as that of dibutyl phthalate over the range 35–75°. The applicability of the molecular still to fractionation of the methyl esters of the organic acids formed by oxidation of bituminous coals has been pointed out.

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[CONTRIBUTION FROM THE COAL RESEARCH LABORATORY, CARNEGIE INSTITITE OF TECHNOLOGY]

Oxidation Products of Certain Petrographic Constituents of Bituminous Coals

BY GEORGE SCHULZ[1] AND H. C. HOWARD

The chemical reactions of the petrographic constituents of coal have been studied by a number of investigators and in some instances wide differences in rate of oxidation or of hydrogenolysis[2] have been reported. An obvious objection to the use of rate measurements as a criterion of chemical difference lies in the great effect that purely physical factors such as surface, porosity and state of molecular aggregation may have on over-all rates of reaction. In this work an attempt has been made to determine, by isolation of degradation products of established structure, what fundamental chemical differences may exist between certain of the petrographic constituents.[3] The method applied consisted of strong oxidative degradation to water soluble acids followed by recovery and esterification of the acids and fractionation of the esters.[4]

Since it is not possible to obtain pure samples of the petrographic constituents, the work was carried out on samples which represented as high a concentration of the particular constituent concerned as it was practical to obtain. The petrographic description and chemical composition of the samples studied are given in Table I. The Pittsburgh Seam coal is predominantly "bright," over 90% anthraxylon and translucent attritus[5]; the sample from the High Splint coal was hand-picked to furnish a high content of opaque attritus, estimated[6] to be 60%; the fusain was hand-picked from the Illinois No. 6 bed[7] and the product from the Utah coal[8] had been separated by flotation and presumably consisted largely of "resins." There are striking differences between these materials in ultimate composition. The atomic carbon–hydrogen ratios range from over 2 for the fusain sample to 0.7 for the resins. The high C/H for fusain points to a large content of highly condensed cyclic structures. A single aromatic ring surrounded symmetrically by three others has a C/H of 1.5; with six surrounding rings the ratio rises to 2.0 and increases slowly as additional peripheral rings are added. The low C/H for the resins shows the presence of considerable hydroaromatic or aliphatic structure; three aliphatic carbon atoms

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(1) Present address: Neville Company, Neville Island, Pittsburgh, Pennsylvania.

(2) Fuchs, Gauger, Hsiao and Wright, *Mineral Industries Penna. State Coll.*, **23** (1938); Yohe and Harman, *Trans. Illinois State Acad. Sci.*, **32**, No. 2, 134 (1939). For a general discussion of effect of type of coal on hydrogenolysis see Lowry, "Chemistry of Coal Utilization," John Wiley and Sons, New York, N. Y., 1945, p. 1757.

(3) Bone and Bard, *Proc. Roy. Soc.* (London), **162A**, 495 (1937), have applied alkaline permanganate oxidation to certain petrographic constituents of three British coals. No significant differences between oxidation products were found, but a very much lower rate of oxidation of fusain was reported.

(4) For methods of oxidation see Juettner, THIS JOURNAL, **59**, 208, 1472 (1937). For methods of esterification and fractionation of the esters see Schulz and Howard, THIS JOURNAL, **68**, 991 (1946).

(5) Fieldner, *et al.*, *U. S. Bur. Mines, Tech. Paper*, **525** (1932).

(6) This was a part of Bureau of Mines sample B3, see *Ind. Eng. Chem.*, **31**, 1160 (1939).

(7) From St. Ellen Mine.

(8) From Hiawatha Mine, Hiawatha, Utah.

TABLE I

CHEMICAL AND PETROGRAPHIC COMPOSITION OF COALS OXIDIZED

		Chemical composition, %								Petrographic composition, %			
											Attritus		
Seam	Mine	C	H	N	S	O	Ash	Moisture	C/H	Anthraxylon	Translucent	Opaque	Fusain
Pittsburgh[a] (bright)	Edenborn	77.4	4.98	1.54	0.99	5.69	7.5	1.9	1.29	50	44	2	4
High Splint[b] (dull)	Clover Splint	76.2	4.20	1.25	0.35	7.30	9.2	1.5	1.51	3	35	60	2
Illinois[c] No. 6 (fusain)	St. Ellen	88.2	2.90	0.46	2.84		4.1	1.5	2.53	Hand-picked sample of fusain			
Hiawatha[d] (resins)	Hiawatha	81.1	9.55	0.20	6.44		2.71	0.0	0.71	Resins—separated by flotation			

[a] Chemical analysis by this Laboratory; petrographic composition shows values for the entire bed, p. 31, ref. 5. [b] Chemical and petrographic analyses from ref. 6. [c] Chemical analysis by this Laboratory. [d] Chemical analysis by this Laboratory, dry basis.

per aromatic ring are required for a ratio of 0.75. The bright coal and the sample rich in opaque attritus have intermediate values of C/H. When thin sections are examined under the microscope, resins and bright coal transmit light easily; the attrital material ranges from "translucent" to "opaque" and the fusain is predominantly opaque. It is probable that the difference in light transmission of the petrographic constituents is reated to the extent of condensation of the carbocyclic structure present. The higher carbon-hydrogen ratios and lower chemical reactivity found for the fusain and opaque attritus are in agreement with this view.

Discussion of Experimental Results

Qualitative differences in the behavior of these materials were noted early in the oxidation. The primary reaction products of the bright coal and the resins, with the fuming nitric acid, were pale yellowish-orange, while those from the splint and fusain samples were brownish-black. All, however, were readily soluble in water and all were converted to pale yellow, hygroscopic, partly-crystalline products by the alkaline permanganate. The data on the yields are summarized in Table II. It has been observed that this drastic oxidation procedure usually results in the destruction of the greater part of any oxalic acid which may have been formed in the earlier stages of the degradation.[4] This was also true of these materials with the exception of the resins where significant amounts of oxalic acid were found even in the final oxidation products. "Total benzenoid acids" represent the difference between the total acids recovered and the oxalic acid found by analysis, calculated to the dihydrate. Mellitic acid was determined by precipitation as the ammonium salt in ammonium hydroxide. Earlier work[9] on synthetic samples has shown the recovery by this procedure to be about 90%.

TABLE II

YIELDS OF ACIDS,[a] %

Coal	Total	Oxalic[b]	Total benzenoid[c]	Mellitic
Pittsburgh (bright)	30.7	2.7	28.0	6.2
High Splint (dull)	36.8	0.0	36.8	13.5
Illinois No. 6 (fusain)	56.3	0.0	56.3	25.4
Hiawatha (resins)	32.9	11.9	21.0	1.5

[a] Weight, % of coal on "dry, ash-free" basis. [b] Calculated as $H_2C_2O_4 \cdot 2H_2O$. [c] A difference figure.

Significant differences between fusain and the other constituents are evident in the yield of total benzenoid acids, and particularly in the amount of the highest member of the series, mellitic. These results are in agreement with the structure indicated by the high carbon-hydrogen ratio of this material. The yield of mellitic acid from fusain is of the same order as that obtained from a 700° coke.[4] The yield of mellitic acid from the sample high in opaque attritus is much lower than that from fusain, but is more than two-fold greater than that from the bright coal, indicating a considerable content of condensed carbocyclic structure. Such a structure would account for the low reactivity which has been reported for the opaque material in hydrogenolysis reactions. The lower total benzenoid and mellitic acid yields of the bright coal reflect the lower carbon-hydrogen ratios and the relatively smaller content of condensed cyclic structures. The very small recovery of mellitic acid from the oxidation products of the resins also is in agreement with the low carbon-hydrogen ratios and the probable high content of aliphatic or hydroaromatic structures.

Samples of the acids recovered after separation of the mellitic acid were esterified with diazomethane and fractionated by exhaustive stepwise distillation in a molecular still. As has previously been observed with oxidation products of bituminous coal,[9] a significant fraction of the methyl esters could not be distilled under conditions where the methyl ester of the highest member of the benzene carboxylic series, mellitic, distills quantitatively. Thus, there are undoubtedly present, even in these products of very drastic oxidative degradation, acids of more complex, or more unstable types of structure, than those of the benzene carboxylic series. With respect to the fraction of methyl esters distillable, the fusain also differs significantly from the other petrographic constituents, some 90% of the esters from the acids from fusain being volatile at not

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(9) Juettner, Smith and Howard, THIS JOURNAL, **59**, 236 (1937).

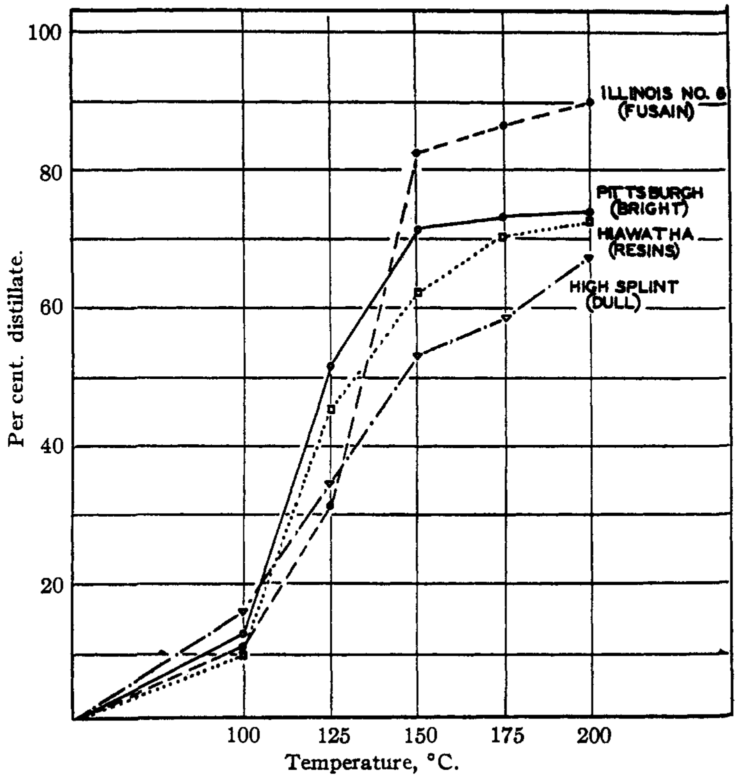

Fig. 1.—Distillation of esters from petrographic constituents.

over 200°, whereas the fraction of the esters of the other constituents volatilized at this temperature ranged from 67 to 75%.

The cumulative per cent. of the esters distilled, as a function of temperature, is shown in Fig. 1. The esters of the acids from the fusain oxidation are characterized by a high content distilling at 150°. The bright coal, relatively, is richest in the 125°-fraction and the sample high in opaque attritus is relatively poor in all, and particularly in the higher temperature fractions.

A summary of the yields of esters and their distribution is given in Table III. Attempts were made to separate and identify crystalline esters in all the fractions, but the amounts so isolated were small. The yields of crystalline material from the esters of the oxidation products of the resins were outstandingly poor. A crystalline mixture of tetra- and pentamethyl esters of the benzene carboxylic series was isolated from the 125°-fractions of the bright coal and the resin samples, and penta and small amounts of hexa from the 150°-fractions of the esters of the high splint and fusain samples.

TABLE III

FRACTIONATION OF ESTERS

Temp., °C.	Pittsburgh (bright), %	High Splint (dull), %	Illinois no. 6 (fusain), %	Hiawatha (resins), %
100	12.9	16.2	11.0	9.9
125	39.2	18.5	20.4	35.4
150	19.2	23.6	51.0	17.1
175	2.1	0.6	5.2	8.0
200	0.6	8.5	2.1	2.1
Residue and loss	26.0	32.6	10.3	27.5

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Summary

Special fractions of bituminous coals selected for their high content of the following petrographic constituents: (a) anthraxylon and translucent attritus, (b) opaque attritus, (c) fusain and (d) resins were oxidized to water soluble acids by fuming nitric acid followed by alkaline permanganate. The yield of total benzenoid acids decreased in the order fusain, opaque attritus, anthraxylon and translucent attritus, resins. The yields of mellitic acid were 25.4, 13.5, 6.2 and 1.5 g. per 100 g. of material on the "dry, ash-free basis," respectively. It has been pointed out that the yield of mellitic acid from the fusain sample is of the same order as that from a 700° coke. Among these materials there is a correlation between mellitic acid yields, carbon–hydrogen ratios and opacity in thin sections. Esterification and fractionation of the mixed esters showed the presence of benzene pentacarboxylic acid in addition to mellitic acid in the oxidation products of fusain and in those from the splint coal. The oxidation procedures used did not disclose any specific chemical differences among petrographic constituents other than those indicated by ultimate chemical analysis.

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