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Reactions of a Bituminous Coal with Sulfuric Acid

by
C. R. Kinney and V. E. Gray*
Fuel Technology Department, The Pennsylvania State University
University Park, Pennsylvania
*E.I. du Pont de Nemours and Company, Inc., Kinston, North Carolina

INTRODUCTION

Bituminous coals react with concentrated sulfuric acid producing useful ion-exchange materials (1,2). The reaction involves oxidation and sulfonation introducing carboxyl and sulfonic acid groups, but otherwise, little is known about the chemical changes that occur in the coal substance (3). Because sulfuric acid is less oxidizing at moderate temperatures than many of the oxidizing reagents that have been used in coal constitution research [nitric acid for example (4)],and has strong cleavage action on ether linkages, the use of this reagent in studying the constitution of coals should be particularly elucidating.

EXPERIMENTAL

The coal selected for study is from the Pittsburgh seam in western Pennsylvania. An analysis is given in Table I. When the coal, ground to minus 200 mesh, and 96.7% sulfuric acid are mixed at -10°C. or below, no observable reaction occurs, but at 0°C. or higher, the temperature of the mixture rises slightly and sulfur dioxide is evolved. The coal has a large absorptive power for sulfuric acid and it requires several times its weight to obtain a fluid mixture. With a ratio of 12 to 1, the coal disperses freely and increases the viscosity of the acid noticeably. The dispersion cannot be filtered through a coarse fritted glass filter using an aspirator pump. Bubbles of sulfur dioxide rise to the surface, but break with difficulty. After reacting for several hours, an undispersed solid product begins to collect on the surface of the acid. It the mixture is now placed in a refrigerator for a time, the liquid sets to a gel. On warming to room temperature, and when stirred, the gel reverts to the original liquid state.

The dispersing action of concentrated sulfuric acid on the coal can be domonstrated in another way. A 1-cm. cube of coal, dried at 100°C. for 2 hours and placed in the acid at 25°C., immediately begins to undergo disintegration. If the process is aided by stirring, the coal can be dispersed readily in this way. When the coal-acid dispersions are diluted with water, flocculation occurs and filtration can be accomplished. The product, after thorough washing, dries to a relatively hard granular mass. At higher reaction temperatures, the product is actually harder than at lower temperatures.

Standard Sulfonation Procedure:--Twenty grams of minus 60-mesh coal are placed in a 1-l., 3-neck flask fitted with a mercury-sealed stirrer, a thermometer, and a delivery tube for removing the sulfur dioxide. Then, 400 g. of 96.7% sulfuric acid are added to the coal and the stirrer started. Temperature of the mixture is maintained by an electric heating mantle regulated by a transformer.

At the end of the heating period the reaction mixture is cooled and poured on ice. The product is filtered through fritted glass and washed repeatedly until 50 ml. of the wash water titrated less than 1 ml. of 0.1 N sodium hydroxide. The product is dried for 12 hours at 100°C., and again washed with water. This removes additional sulfuric acid. No doubt the samples still retain small amounts of uncombined acid, because they give 0.5% to 2.0% sulfate sulfur, and 0.5% to 1.0% more pyritic sulfur than the original coal, when analyzed by the standard A.S.T.M. method for coals.

Analysis:--Carbon and hydrogen analyses listed in Table II are macro determinations, and the nitrogens are macro Kjeldahls. The sulfur values given in Tables II and III are standard A.S.T.M. determinations of sulfur in coals. The total carbon lost by sulfuric acid treatment, given in Table II, is the difference between the per cent of the original carbon left in the product, calculated from its weight and per cent carbon, and 100%. The surface areas were obtained by the B.E.T. method using nitrogen (5).

DISCUSSION

Yields of product coal obtained at different temperatures from 25° to 150°C. vary from 115% to 125%. From the data given in Table II, it appears that at low temperatures, 25° to 50°C., several days of treatment are required to obtain the maximum yield of 120% to 125%. Only one day is needed at 100° to 110°C. When the reaction is continued beyond the time of maximum yield, 115% to 117% yields result. At this level the product becomes resistant to further loss by continued treatment. Greater precision of the yields would have been obtained had the reaction temperature been maintained more closely. At times the temperature varied by as much as 10°C. because of line voltage variations.

The composition of the products is remarkably constant, both at a given reaction temperature and for a range of temperatures from 25° to 150°C. Table II shows that the per cent carbon of the original coal falls from 82.3% to about 61.6% ±2% under these conditions. A considerable part of this decrease in carbon content is caused by the increased weight of product, but at the same time about 13.3% ±3% of the original carbon of the coal is eliminated, partly by oxidation to carbon dioxide.

The hydrogen content of the coal falls much more than the carbon percentage-wise--from 5.6% to about 2.6% ±ca.1%, if the hydrogen analyses of the 50°C. products in Table II, which seem to be out-of-line, are excluded. This loss of hydrogen is similar to that observed when like coals are oxidized by nitric acid (4) or air (6), and may be accounted for by oxidation because of the evolution of sulfur dioxide. A low atomic hydrogen-carbon ratio of the products of about 0.4 shows that their structure must be that of a polynuclear aromatic, or more likely, quinoid type (7).

The nitrogen analyses in Table II show that almost all of the nitrogen of the original coal is retained in the products, keeping in mind that the latter weigh about 120% of the coal. If the structure of the products is essentially polynuclear or quinoid in character, it follows that the nitrogen atoms of the coal are present in ring structures, substituting for carbon atoms, and thus surviving the oxidative conversion of the rings to the final product.

Also included in Table II are data on the per cent of organic sulfur in the products. This non-sulfatic, non-pyritic sulfur would include organic sulfur of the original coal, although some may have been removed by the sulfuric acid treatment. The data show that a significantly constant amount of sulfur is introduced regardless of the conditions of treatment. Slightly larger amounts are introduced under milder conditions, that is, lower temperatures. At 25°C. the per cent of sulfur decreases with longer reaction times, suggesting that certain structures in the raw coal, such as hydroxyl groups, react but are subsequently oxidized with the loss of the sulfur-containing group. The fact that increasing the temperature of treatment does not introduce additional sulfur groups suggests that the structure of the product is not reactive toward sulfuric acid. This also favors the polynuclear quinoid structure (7) rather than aromatic.

The main sulfur-introducing reaction proceeds readily at 25°C. and to a greater extent than at 150°C. This temperature effect is typical of addition reactions, although it is possible that easily sulfonated structures, such as phenolics, are sulfonated similtaneously. This would inhibit further sulfonation in the immediate vicinity of the sulfonic acid group introduced. A likely structure for the addition-type of reaction would be unsaturated rings which, following the addition of the acid, could indergo oxidation to aromatic or quinoid structures and thus incorporate the sulfur-bearing group into the oxidation-resistant product. The sulfonated phenolics would also be expected to be oxidized to quinoid structures subsequently.

Considering the dispersing action of concentrated sulfuric acid on the coal and the fact that some 13% of the carbon is removed, an examination of some of the physical properties of the product is of importance. Of particular importance for ion exchangers is large surface area. Surface areas of the products obtained under various conditions show that both temperature and time of treatment increase the area markedly, Table II. At 25°C. surface areas are smaller than the original coal, which suggests that the treatment actually seals off pores. At higher temperatures, increased areas indicate increased dispersion and development of new surfaces.

A particularly attractive hypothesis to account for the observed dispersive action of sulfuric acid and increased surface areas is that the acid molecules force their way between the coal lamella (8) during the process of dispersion. This would account for the difficulty of filtering, the gelling on cooling, and the increased surface areas on removing the acid. However, the interlayer spacing of the crystallites of the products actually decrease with increasing surface area. Thus the d-spacing of the raw coal decreases from 3.93A. to 3.66A. when the coal is treated at 110°C. for 1 day and to 3.52A.

after 8 days; meanwhile the surface area increases from 2.7 m^2/g. to 4.5 m^2/g., then to 183 m^2/g. These results indicate that the lamella draw together rather than separate during the acid treatment. Crystallite heights of the raw coal and the 110°C. products are all 7-8A., indicating that the crystallites are but two lamella thick on the average (9).

The action of concentrated sulfuric acid on the mineral matter of the coal is also significant. At 25° to 50°C. the ash content of the coal falls from 8.2% to about 5.5%, see Table III. This is mainly caused by the extraction of soluble sulfates by the acid and subsequent washing. The sulfate sulfur is undoubtedly adsorbed sulfuric acid displaced by hydrochloric acid in the A.S.T.M. procedure. Similarly the cold dilute nitric acid used to determine pyritic sulfur displaces additional sulfuric acid, giving values for pyritic sulfur greater than in the original coal.

The pyrite is attacked by the hot sulfuric acid beginning at 100°C. and completely at 110° to 150°C. This results in a noticeable drop in the percentage of pyritic sulfur and of ash at these temperatures, Table III. The remaining "pyritic sulfur" is believed to be adsorbed sulfuric acid removed by the dilute nitric acid treatment.

In general low "sulfate sulfur" (less than 1.0%) seems to predict that the product will have a large surface area (Table III). No proof is available but it seems to be possible that a high degree of dispersion in sulfuric acid, which leads to a large surface area, might result in a product from which the adsorbed sulfuric acid might be desorbed more easily, on the basis that originally small pores are converted to large ones.

SUMMARY

A high-volatile A bituminous coal reacts with concentrated sulfuric acid, in the range of 25° to 150°C., with the loss of about 13% of its carbon partly as carbon dioxide. Over 50% of the hydrogen is removed, but nearly all of the nitrogen remains. About 5% sulfur is introduced. The composition of the product indicates that it has a polynuclear quinoid type of structure. The crystallites are two lamella high on the average, as in the raw coal, and their interlayer spacing is about that of many chars and carbons. Maximum surface area is developed by prolonged treatment at higher temperatures.

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TABLE I

ANALYSIS OF THE COAL

Constituent	As Received	D.A.F. Basis
Moisture	2.01%	-
Ash	8.04	-
Vol. Matter	36.44	40.51
Carbon	74.02	82.29
Hydrogen	5.29	5.63
Nitrogen	1.16	1.28
Sulfur	2.26	2.51
Cal. Value	13,192 Btu	-

TABLE III

ANALYSIS OF THE PRODUCTS

Conditions of Sulfonation		Analysis, Dry Basis, %				
Temp., °C.	Time, days	Ash	Total S	Sulfate S	Pyrite S	Org. S
Raw Coal		8.2	2.5	0.2	1.0	1.3
25	5	5.9	9.2	1.5	1.8	5.9
	10	5.8	9.4	1.6	1.2	6.6
	20	5.7	9.2	1.8	1.8	5.6
	31	6.3	8.4	1.2	1.9	5.3
50	1	5.9	8.4	1.9	1.8	4.7
	3	5.7	8.6	1.6	2.0	5.0
	5	5.5	9.0	2.4	1.5	5.1
	8	5.4	8.4	1.7	1.7	5.0
100	1	5.4	8.2	1.6	1.2	5.4
	2	5.3	7.2	1.3	1.2	4.7
	5	4.9	7.0	1.2	1.0	4.8
	8	4.9	6.4	0.7	0.8	4.9
110	1	4.8	7.8	2.1	0.9	4.8
	3	4.5	6.1	0.7	0.7	4.7
	8	6.7[a]	5.7	0.6	0.2	4.9
150	1	4.5	6.3	1.1	0.3	4.9
	3	4.3	5.8	0.5	0.5	4.8

[a] The ash content of a duplicate run was 4.5%

TABLE II

SULFONATION DATA

Conditions of Sulfonation		Yield	Analysis, Dry Ash-Free Basis, %				Total C Lost on Treatment,%	Surface Area m²/g.
Temp.,°C.	Time,days	%	C	H	N	Org. S		
Raw Coal		-	82.3	5.6	1.3	1.3	-	2.7
25	5	116	63.6	3.5	1.0	6.2	11.2	2.3[a]
	10	117	62.8	2.0	1.0	6.4	13.2	0.002[a]
	20	120	63.1	2.1	0.9	5.9	10.5	0.12[a]
	31	116	63.8	2.6	1.0	5.7	10.4	1.5
50	1	119	62.0	6.5	0.9	5.0	11.6	3.1
	3	117	61.5	5.6	0.9	5.4	13.5	16.
	5	125	59.7	3.1	0.9	5.4	11.6	-
	8	122	60.7	3.6	0.9	5.2	10.1	54.
100	1	120	61.4	2.6	0.9	5.7	13.5	7.2
	2	116	61.0	4.6	0.8	5.0	13.9	101.
	5	117	60.6	3.1	0.9	5.0	12.7	-
	8	115	62.1	2.6	0.9	5.2	12.7	222.
110	1	123	59.6	2.6	0.9	5.0	12.3	4.5
	3	115	61.2	2.6	0.9	4.9	13.2	158.
	8	116	60.8	2.0	0.9	5.3	16.5	183.
150	1	115	61.3	3.3	1.0	5.1	16.2	178.
	3	117	62.8	2.6	1.0	5.0	13.8	272.

[a] These surface areas were very kindly made by J.R. Malone