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OXIDATION OF COAL

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This invention relates to the oxidation of coal, and more particularly to oxidation of coal for the purpose of rendering its content of non-fusain organic matter soluble in organic solvents containing heterocyclic oxygen.

Patent No. 2,242,822, granted May 20, 1941, on an application filed by me, discloses and claims my discovery that when coal in a mildly oxidized condition is treated with an organic solvent containing heterocyclic oxygen the non-fusain organic matter is dissolved by the solvent while the fusain and mineral matter, or ash, remain undissolved. Thereby the dissolved carbonaceous matter can be recovered apart from fusain and in an ash-free form. Furfural is preferably used as the solvent in the practice of that invention, and it will be referred to hereinafter as typifying the designated class of solvents.

The state of oxidation of the coal is that in which it contains hydroxycarboxylic acids. The patent describes the preferred use of nitric acid for that purpose. That acid does convert the coal to a state in which it is furfural soluble, and it does so quickly, as is desirable. However, large amounts of acid relative to the weight of coal treated are necessary, so that such nitric acid oxidation of coal is rather expensive. The patent mentions the possibility of effecting the oxidation with air, but simple air oxidation is so slow as to be economically undesirable, and I have found that even when a catalyst is used to expedite the oxidation, the maximum solubility is not developed.

A major object of this invention is to provide a process of oxidizing coal with air that is relatively rapid, simple to perform, and inexpensive.

A further object is to oxidize coal with air to reduce its equivalent weight and produce sufficient active hydroxycarboxylic acid groups to render the non-fusain organic matter soluble in organic solvents containing heterocyclic oxygen.

Yet another object is to provide a process of preparing coal for extraction with organic solvents containing heterocyclic oxygen which involves preliminary oxidation with air followed by treatment with nitric acid, which achieves the results described in the above-identified patent but requires much less acid and is performed more quickly than the air oxidation described therein.

A special object is to provide a catalytic method of oxidizing coal with air.

Still another object is to provide a method of increasing the acid strength of coal which has been oxidized to produce hydroxycarboxylic acid groups.

Other objects will appear from the following description.

I have now discovered, and it is upon this that the invention is in part predicated, that acid groups, such as hydroxycarboxylic groups, may be introduced into coal by subjecting it to the action of an oxygen-containing gas, suitably air, while heated to an elevated temperature, and then heating it in contact with air or other oxygen-containing gas at a lower temperature. The first heating step oxidizes the coal mildly with production of acid groups, and the percentage of such groups is increased in the second heating stage.

I have discovered further that particularly beneficial results attend the use of an oxidation catalyst, especially in the second heating stage. For this purpose I prefer to use ammonium nitrate, although other substances may be used also, e. g., potassium nitrate, oxides and salts of chromium, manganese, vanadium, iron, cobalt and nickel, or bases such as potassium, sodium and ammonium hydroxides, and organic bases.

The exact temperatures to be used will depend in part upon the particular coal being treated, the extent of oxidation desired, whether or not a catalyst is used, the time of exposure, and related factors. The coal should not be heated to a temperature high enough to cause carbonization, and generally speaking it should be heated at least to 120° C. but not over about 350° C. Using ammonium nitrate as the catalyst, satisfactory results are had by first heating for 30 minutes in air at 280° to 350° C., and conducting the second heating at 150° C. Likewise, fixed proportions for all catalysts can not be set. However, it may be said that generally speaking 1 per cent or less of catalyst suffices. For example, there may be used from 0.5 to 5 parts of NH_4NO_3 per 100 parts of coal, both by weight.

The extent to which acid groups are introduced into the coal can be determined readily. Into an Erlenmeyer flask equipped with a reflux condenser there are placed 0.5 gm. of coal sample, 1 cc. of alcohol, 15 cc. of water, and 25 cc. of n/10 sodium hydroxide solution. The mixture is boiled for 30 minutes, then filtered, and the filtrate titrated with n/10 hydrochloric acid, using phenolphthalein. Where the oxidation has been so extensive as to make the filtrate too dark to titrate accurately, the procedure is modified by adding 25 cc. of n/10 calcium chloride solution

just before filtration, to precipitate calcium humate.

In the first stage the coal may be passed through a rotary furnace countercurrently to a stream of air, and depending upon the length of exposure it may be passed through one or more times. Generally speaking, the longer the exposure the greater the percentage of acid groups. To oxidize the coal sufficiently for use in the invention of my above described patent, the coal after treatment should contain acid groupings equivalent to at least 4 cc. of normal sodium hydroxide solution per gram of coal.

As exemplifying this aspect of the invention, a number of coal samples were oxidized in air at 280° to 350° C. to the extent shown in the following table. 500 gm. of each sample were mixed in a porcelain dish with 100 cc. of a 25 per cent solution of NH_4NO_3. The mixture was stirred constantly and brought to dryness by heating on an electric plate to about 150° C., and agitation was continued until white fumes were no longer given off. This required 30 to 75 minutes. The increase in acid groups is evidenced by the following data:

Sample untreated	Before treatment	After treatment
	Cc. of n/10 NaOH	
#1	1.8	11.6
#2	10.2	25.0
#3	20.5	38.6
#4	20.5	37.4
#5	20.5	39.2

It is characteristic that as this oxidation of coal with production of acid groupings progresses, the equivalent weight of the coal decreases progressively. In this manner the equivalent weight can be decreased from about 10,000 for the original coal to 300, or less. Where the coal is to be treated by the process of my aforementioned patent it is desirable to extend the oxidation until the equivalent weight of the coal is from 300 to 200, especially for reasons presently to appear.

Simple oxidation as described hereinabove may suffice for some purposes, but the product does not give fully desirable results when treated with furfural because, as I have found, it lacks acid strength. This is so despite the presence of a large number of acid gorups.

The acid groups produced as described above, e. g., carboxyl or phenolic hydroxyl groups, are potentially capable of giving hydrogen ions, but the actual degree of ionization may vary from zero to 100 per cent. There is no simple means for determining the electrolytic dissociation constant of the solid oxidized coal but it may be determined by a comparative method, and for the purposes of this invention acetic acid is suitably taken as the basis of comparison.

For this purpose there are placed in an Erlenmeyer flask equipped with a reflux condenser 0.5 gm. sample of oxidized coal and 25 cc. of a n/10 calcium acetate solution. The mixture is boiled 30 minutes, cooled and filtered, and the residue washed with water. The acetic acid liberated is then titrated with n/10 sodium hydroxide solution, using phenolphthalein. The amount of acid liberated is, of course, a measure of the acid strength of the oxidized coal relative to that of acetic acid.

Determined in this way it is found that coal oxidized as above has very low acid strength. Its acid strength may be increased, however, and the invention is further predicated on this, by treatment with nitric acid. In this manner oxidized coal having an acetate number (cc. of n/10 calcium acetate decomposed) of, for example, 3 to 7, may be increased to 25, or more. Although treatment with nitric acid increases the acid strength, there is no apparent further increase in the number of acid groups.

As exemplifying this feature of the invention, 100 gm. of oxidized coal having an alkali value (measure of percentage of acid groups) of 39 and an acetate value of 7 were placed in an Erlenmeyer flask immersed in cold water and 100 cc. of nitric acid (conc.) were added in four portions. After the first violent reaction had subsided, the mixture was heated in a boiling water bath for 1 to 2 hours, then diluted with water, filtered through a Buchner funnel, washed free from nitric acid, and air dried. The product weighed approximately 120 gm. and about 90 per cent by weight was soluble in furfural.

I have found that the lower the equivalent weight, i. e., the higher the percentage of acid groupings, and the higher the acid strength of the oxidized coal before subjecting it to the nitric acid treatment, the less is the amount of nitric acid required to increase the acid strength. By way of illustration, another sample of oxidized coal having an alkali value of 29 and an acetate value of 3 was treated the same as in the example just given. To produce the same weight of product of the same furfural solubility required the use of 250 cc. of nitric acid (conc.).

For rendering oxidized coal quickly soluble in furfural, the coal should be treated to have an acid strength exceeding that of acetic acid.

According to the provisions of the patent statutes, I have explained the principle and method of practicing my invention and have described what I now consider to represent its best embodiment. However, I desire to have it understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

I claim:

1. That method of oxidizing coal which comprises heating the coal in air to an elevated temperature below that which causes carbonization of the coal and thereby producing acid groups in the coal, and then heating the coal in air at a lower temperature and thereby increasing the number of said groups.

2. That method of oxidizing coal which comprises heating the coal in air to a temperature between about 280° to 350° C. and thereby producing acid groups in the coal, and then heating the thus-treated coal in air at a lower temperature and thereby increasing the number of said groups and reducing the equivalent weight of the coal to about 250 to about 300.

3. A method according to claim 1 in which the coal is mixed with a catalyst in the second heating step.

4. A method according to claim 1 in which the oxidized coal is finally treated with nitric acid whereby its acid strength is increased.

5. That method of oxidizing coal which comprises heating the coal in air to not over about 350° C. and thereby producing acid groups in the coal, then heating it at a lower temperature in air and thereby increasing the percentage of said groups, and then treating the oxidized coal with nitric acid and thereby rendering the non-

fusain organic matter of the coal soluble in furfural.

6. That method of oxidizing coal which comprises heating the coal in air to about 280° to 350° C. and thereby producing acid groups in the coal, then mixing it with ammonium nitrate and heating it to a lower temperature and thereby increasing the percentage of said groups, and then heating it with nitric acid and thereby rendering the non-fusain organic matter of the coal soluble in furfural.

7. A method according to claim 6 in which in the second heating step the coal is mixed with about 0.5 to 5.0 per cent of said nitrate and the mixture heated to about 150° C.

8. That method of oxidizing coal which comprises heating it in air to a temperature short of that productive of carbonization to produce acid groupings in the coal sufficient to neutralize at least 4 cc. of normal sodium hydroxide solution per gram of coal and then heating the oxidized coal with nitric acid and increasing its acid strength sufficiently to decompose at least 3 cc. of normal calcium acetate solution per gram of coal.

9. That method of oxidizing coal which comprises heating it in air to about 280° to 350° C. and thereby producing acid groupings in the coal, then heating it in air with ammonium nitrate at a lower temperature and thereby increasing said groupings sufficiently to neutralize at least 4 cc. of normal sodium hydroxide per gram of coal, and then heating the oxidized coal with nitric acid and thereby increasing its acid strength to exceed that of acetic acid.

10. A method according to claim 9 in which said heating with ammonium nitrate is at about 150° C.

11. That method of preparing coal for extraction with an organic solvent containing heterocyclic oxygen which comprises oxidizing the coal by heating it in air and thereby providing acid groupings in the coal and reducing its equivalent weight to not over about 300, and then heating the oxidized coal with nitric acid and increasing its acid strength to exceed that of acetic acid.

12. That method of oxidizing coal which comprises heating the coal in air to an elevated temperature below that which causes carbonization of the coal and thereby producing acid groups in the coal, and then heating a mixture of the coal and ammonium nitrate in air at a lower temperature and thereby increasing the number of said groups.

13. That method of oxidizing coal which comprises heating a mixture of the coal and ammonium nitrate in air first to a temperature not over about 350° C. and thereby producing acid groups in the coal, and then at a lower temperature and thereby increasing the percentage of said groups, and then treating the thus oxidized coal with nitric acid and thereby rendering the non-fusain organic matter of the coal soluble in furfural.

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