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DESULFURIZED CHAR WITH PHOSPHORIC ACID

Joseph G. Santangelo, Brookville, Pa., and Thomas P. Dorchak, Nabnasset, Mass., assignors to Kennecott Copper Corporation, New York, N.Y.

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ABSTRACT OF THE DISCLOSURE

Crushed coal may be desulfurized by slurrying with a phosphoric or phosphorus acid or mixture thereof, removing excess liquid, and heating the mixture at an elevated temperature to drive the sulfur from the coal.

FIELD OF INVENTION

There are at present no commercial means of removing sulfur from coal more economically than stack gas scrubbing. This is due to the complex nature of coal itself. The sulfur of high-sulfur coals occurs in two major forms; namely, very finely divided pyrite particles dispersed throughout the coal and organic sulfur which is also somewhat uniformly distributed throughout the coal. Mechanical cleaning or washing the coal will at best remove only part of the dispersed pyrite from even finely crushed coal but none of the organic sulfur. Leaching or chemical attack may remove most of both forms, but again only from finely crushed coal, and at high cost. Thermal attack (pyrolysis) in the absence or presence of various agents which remove sulfur has not attained commercial operation because of the great tendency of hot carbon to fix sulfur as very stable organic sulfur compounds. Separation of sulfided grabbers from char is also very difficult. Liquefaction and de-ashing have also not been demonstrated commercially although desulfurization of coal-derived liquids and gases involves well-known proven commercial petroleum technology.

It is highly desirable, and frequently held essential, that the sulfur content of char be low whether used in metallurgical processes or as a fuel. Under conventional charring conditions, it is necessary to use a low sulfur coal in order to obtain a product containing relatively low sulfur values. Inasmuch as reserves of such low-sulfur coal are limited, it would be desirable to have technology for removing a greater portion of the sulfur from coal during the charring process than is now available to such manufacturers.

PRIOR ART

Over the years the desirability of removing the sulfur content of coals during the coking process has been known. For example, an 1899 U.S. patent issued to J. W. Kenevel (618,104) describes a process whereby coal to be treated is charged to a suitable retort and sufficient heat applied to cause liberation of the volatile elements. As those elements are liberated jets of steam or hot air carrying a small percentage of a vaporized acid solvent for sulfur is discharged into the body of coal. This acid solvent is stated to be acetic acid. In 1908 Stoner, in U.S. Pat. No. 887,145, treated coke made from coal containing sulfur to an action of chlorinating gas, i.e. hydrochloric acid to remove the inorganic sulfur from the coal. Stoner recognized that the organic sulfur remained for the most part in the coke and is not removed by the hydrochloric acid gas.

U.S. Pat. No. 1,098,359 teaches the adding of such phosphorus compounds as lime phosphate, phosphate chalk or apatite, to coal prior to coking. The purpose of this addition was to form a ferro-phosphorus compound so that any iron in the coke would be deprived of taking

up any further sulfur in the coking process. U.S. Pat. No. 2,057,486 teaches the use of hydrochloric acid in desulfurizing coal. U.S. Pat. No. 2,166,321 discloses a method where a carbonizable extract of coal is produced. The extract is then treated with diluted inorganic acids and finally the extract is coked in the absence of the acids. Other inventors have attempted to produce low sulfur containing coke by carbonizing in a moving stream of reducing gases. See for example U.S. Pat. No. 3,117,918.

Thus it is seen over the years that many have attempted in one form or another to remove sulfur from coal, char and coke. Attempts have been made to accomplish the sulfur removable prior to the carbonization process, during the carbonization process, and after the carbonization process. In all cases as far as we are aware the product still contained a significant quantity of sulfur.

SUMMARY AND OBJECTS

It is, therefore, the principal purpose of this invention to provide a process for the removal of sulfur during the production of char from coal.

The term "char," as used herein, in contradistinction to the usual coke product is characterized as the solid carbonaceous residue of coal which has been distilled between about 400 and 800° C. and containing residual volatile matter of at least about 5% by weight. Coke, on the other hand, normally contains less than about 2% by weight volatile matter and is the product of destructive distillation of coal at temperatures above about 1000° C. Char may find particular use by power companies in the generation of electricity. A low sulfur char will substantially assist in reducing atmospheric pollution normally caused by utilization of coal for such purposes.

It has long been recognized that sulfur in coal exists in several forms. For example, sulfur may be found in coal in the form of pyrites, gypsum or calcium sulfate and organic sulfur. Organic sulfur is combined with the carbon hydrogen and oxygen of the coal. Organic sulfur is believed to be associated directly with the carbonaceous matter by incorporation of the sulfur atoms into the aromatic molecular structure, although the particular way in which the sulfur is bound in the molecular structure is not known. It is believed that the removal of organic sulfur by hydrogen is a reversible reaction. This reaction is

$$(C){-}S + H_2 \leftrightarrows (C) + H_2S$$

Sulfur is transferred from the gas phase to the carbonaceous phase at relatively high ratios of hydrogen sulfide to hydrogen. Thus it is apparent that the removal of organically bound sulfur from coal is difficult in view of this reversible reaction.

Applicants have found that a significant quantity of the organic sulfur and substantially all of the inorganic sulfur can be removed from coal during the carbonization process. Such a process comprises the steps of mixing crushed coal with an acid selected from phosphoric acids, phosphorous acids and mixtures thereof, removing the excess acid, if any, from the mixture and heating the mixture to a temperature of between about 400 and about 1100° C. for at least about 15 minutes.

Using applicants' novel process, experiments have shown that sulfur could be reduced to as low as 1.7% from a 3.0% sulfur, Western Kentucky No. 11 coal. From a 4.3% sulfur containing Illinois No. 6 coal, a char of 2.76% sulfur content can be produced. From a 6.7% sulfur containing Missouri coal, a char of 3.3% sulfur content can be produced. For comparison purposes, using conventional coal desulfurization processes, the sulfur content of chars produced from these respective coals would be approximately 2.0% sulfur, 3.0% sulfur, and 4.8% sulfur. While on first glance this increase in sulfur removal does not appear to be large, if the number of tons of coal and char used is taken into consideration, it is apparent that even a small decrease in sulfur becomes significant when considered as a pollution abatement measure.

DESCRIPTION

The applicants, in their experiments, have learned that orthophosphoric acid, commonly called phosphoric acid and any of the polyphosphoric acids or phosphorus acids or mixtures thereof may be used. The polyphosphoric acids may be represented by the formula $H_{n+2}P_nO_{3n+1}$ wherein *n* is greater than 1. Examples of these polyphosphoric acids are metaphosphoric acid pyrophosphoric acids. As used hereinafter the term phosphoric will be used and it is to be understood that all such phosphoric acids, phosphorus acids and mixtures thereof, described above can be used.

In the preferred embodiment of this invention a 5 or 10% aqueous solution of phosphoric acid is slurried with crushed coal. The slurry is then filtered to remove excess acid. After filtration the coal will contain from about 10 to about 30% liquid based on the weight of the coal. Twenty weight percent liquid on the crushed coal is preferred. Experiments have shown that as little as 0.25 weight percent phosphoric acid based on the coal weight can be used in effecting the removal of sulfur from the coal during the carbonization thereof. Amounts of phosphoric acid up to about 25% by weight on the coal or more may be used. However the preferred range for economic consideration is between about 1 and about 5% based upon the weight of the coal. The coal is crushed in any convenient manner in crushers or grinding mills. Preferably the coal will be reduced to a size between about 100 and 10 mesh U.S. Sieve Series. Larger particles of coal may be desulfurized using this invention but the time at temperature is thereby increased.

The coal, after it has been slurried with phosphoric acid and the excess acid, if any, removed therefrom, is fed to a suitable vessel for heating. The coal-phosphoric acid mixture may be heated to a range of between about 400 and 1300° F. with the preferred range being between 700 and 1200° F. Although the time taken to heat the coal slowly up to the desired temperature appears to have a minimal effect on the sulfur removal, it is preferred to heat at a relatively slow heating rate. It appears that a slow heating rate allows the sulfur compounds to leave the coal while charring is proceeding in a uniform and effective manner. It is believed that the most rapid sulfur removal occurs at around 700° F. At this temperature the evolution of volatile matter, including some organic sulfur compounds, begins together with pyrite decomposition to pyrrhotite. Once the selected temperature has been reached it should be maintained for a period of time of at least 15 to 30 minutes or longer.

During the heating of the coal-phosphoric acid mixture, it is preferred to maintain an inert or a mildly oxidizing atmosphere in the heating vessel. The inert atmosphere may be carbon dioxide or an atmosphere of spent gas from a coal combustion. Once the selected temperature has been reached a reducing atmosphere is introduced into the vessel. Preferably the reducing atmosphere is a continuously changing one in order to remove the sulfur compounds as they are released from the charring coal. The reducing atmosphere may be any combination of hydrogen, carbon monoxide, methane and an inert gas such as nitrogen. A convenient way in reducing atmosphere is to feed steam and carbon monoxide simultaneously into and through the heating vessel.

During the heat up, charring and cool down periods, it is preferred to use a flowing gas in the reactor vessel. More efficient sulfur removal is obtained since the volatile sulfur compounds such as SO_2, H_2S, etc. is carried off in the gas stream. Preferably the gas in the reaction vessel will be changed every few seconds such that the gas space velocity will be between about 0.1 and 1.0.

After the charring period the char is then allowed to cool down in an inert atmosphere, as previously described. Of course it is recognized that a reducing atmosphere may be used at all times, during the process of this invention, without departing from the scope thereof. However, for economic considerations, by using an inert or mildly oxidizing atmosphere during the heat up and cool down periods significant savings can be realized.

In order to more clearly disclose the nature of the present invention, the following examples illustrating the invention are disclosed. It should be understood, however, that this is done solely by way of example and is intended neither to delineate the scope of the invention nor limit the ambit of the appended claims. In the examples which follow, and throughout the specification, the quantities of materials are expressed in terms of parts by weight, unless otherwise specified.

Example 1

Fifteen grams of Western Kentucky #11 coal was ground to a minus 100 mesh and slurried with 12 milliliters of an aqueous 5 or 10% phosphoric acid solution for 15 minutes. The slurry was then filtered to remove excess acid and approximately half of the sample was weighed into a silica boat inside a tubular furnace. The furnace train consisted of compressed gas tanks, a regulator, a flow meter, a tube reactor, tar traps and a cadmium scrubber. The flowing gas was set to 360 mls./min. through the 18" x 0.8" inside diameter quartz tube reactor. The inert gas was pre-purified nitrogen and the reducing gas consisted of 5.5% hydrogen, 23.6% carbon monoxide, and the balance argon. The furnace was turned on and brought to 500° C. in about 15 minutes and held there for an additional 15 minutes. The results are tabulated below.

		Experimental conditions		
		Run 1	Run 2	Run 3
		Reducing gas, 7.3% phosphoric acid	Reducing gas, 14.6% phosphoric acid	Inert gas, 14.6% phosphoric acid
		Sulfur analysis (weight percent)		
		Char		
	Coal	Run 1	Run 2	Run 3
Sulfate sulfur	0.04			
Organic sulfur	1.97	1.77	1.70	1.56
Pyritic sulfur	1.01	0.11	0.06	0.62
Total sulfur	3.02	1.89	1.76	2.18
Char Yield percent		63.7	66.9	67.2

Example II

A twelve gram sample of Illinois No. 6 coal containing 4.33% by weight sulfur was crushed and slurried with 15 milliliters of 10% phosphoric acid. Excess acid was filtered off and the sample washed with water and dried. The sample was not subjected to the thermal treatment but was analyzed for sulfur. The final total sulfur content was found to be 4.16%.

This example shows that only an insignificant quantity of the sulfur is removed by the phosphoric acid alone. Thus it follows that the phosphoric acid pretreatment materially assists in removing the sulfur during the later thermal treatment.

Example III

Illinois No. 6 coal containing 4.33% by weight sulfur was crushed and 15 gram samples thereof slurried with 12 milliliters of 10% phosphoric acid. The excess liquid was filtered off and the wet cake dried. The wet cake was then carbonized in a reducing gas consisting of about 11% hydrogen, 22% carbon monoxide, and 67% argon in a tube furnace at the temperatures shown in the tabulation below.

		Percent		
Reagent	Max. temp., ° F.	Char yield	S in char	Total Sulfur removal
10% H_3PO_4	930	73	3.23	46
10% H_3PO_4	1,110	71	2.76	55

liquid was filtered off and the coal carbonized by heating to 930° F. in nitrogen. From 930° F. to 1100° F. the coal was carbonized in a reducing gas consisting of 67% argon, 22% carbon monoxide, and 11% hydrogen. The tabulation below shows the results. The tabulation below also shows the acid weight percentages calculated from the original acid concentrations used times the percentage of liquid remaining in the wet coal after filtration (about 20% liquid by weight of filtration).

Run number	Acid and wt. percent on coal as fed to furnace	Coal, percent S	Char, percent S	Char, percent S/coal, percent S	Percent total S removed	Char yield, wt. percent
14	1% H_3PO_2 plus 0.25% H_3PO_4	3.52	1.65	0.47	67.7	69
15	0.75% H_3PO_2 plus 0.25% H_3PO_4	3.52	1.70	0.48	66.7	69
16	0.5% H_3PO_2 plus 0.25% H_3PO_4	3.52	1.90	0.54	63.9	67
17	0.25% H_3PO_2 plus 0.25% H_3PO_4	3.52	2.04	0.58	61.8	66
18	0% H_3PO_2 plus 0.25% H_3PO_4	3.52	2.22	0.63	57.8	67
19	2% H_3PO_4	4.23	2.32	0.55	67.1	*60
20	2% H_3PO_2	4.23	2.28	0.54	67.6	60
21	1% H_3PO_4 plus 1% H_3PO_2	4.23	2.28	0.54	71.4	53
22	16% H_3PO_4	4.06	2.08	0.51	65.2	68
23	16% H_3PO_4	3.56	1.86	0.52	64.4	68

*Estimated char yield.

Example IV

Further experiments on treatment of coal with phosphoric acid were conducted in a packed bed. Two 150 gram lots of 10 x 35 mesh (4.0% sulfur) and 60 x 100 mesh (4.3% sulfur) coal were taken from a larger lot of Illinois coal. These samples were slurried with 120 mls. of 10% phosphoric acid and stirred for 15 minutes. The slurry was filtered and the wet solids dried at 220° F. to drive off excess water but to leave the acid in the coal. Fifteen gram portions of these samples were then carbonized in the packed bed. The samples in the packed bed were heated from room temperature to about 700° F. using a carbon dioxide atmosphere. Since this atmosphere is slightly oxidizing, it was expected to open up the pore structure of the coal making it more reactive. When the packed bed reached 750° C. the atmosphere was charged to a reducing one containing 11% hydrogen, 22% carbon monoxide and 67% carbon dioxide. This atmosphere was retained up through the maximum temperature. The reducing gas or inert gas is desirable above the 750° F. range in order for the coal not to be oxidized or burnt away. After a sufficient amount of time at the maximum temperatures, shown on the tabulation below, the atmosphere was again changed to carbon dioxide and allowed to cool. It was expected that during cooling the carbon dioxide atmosphere would oxidize the remaining pyrrhotite sulfur to iron oxides and sulfur dioxide which would be carried off in the gas stream. The results of these experimental runs are tabulated below.

TABLE

						Percent			
Run No.	Coal mesh size	Weight percent H_3PO_4 on coal	Gas space velocity, $sec.^{-1}$	Heat-up rate of ° F./min.	Max. temp., ° F.	B.t.u. yield	S in char	Total S removed	Char, percent S/coal, percent S
51	10 x 35	2	0.17	18	950	70	3.21	44.7	.79
54	50 x 100	2	0.50	18	950	71	2.93	48.8	.69
47	60 x 100	2	0.17	36	950	72	2.87	49.2	.68
49	60 x 100	2	0.17	36	950	62	2.81	57.1	.66
46	10 x 35	2	0.50	36	950		3.44	39.1	.85
50	60 x 100	2	0.17	18	1,110	66	2.74	55.5	.64
52	10 x 35	2	0.50	18	1,110	67	2.43	59.9	.60
53	10 x 35	2	0.50	18	1,110	69	2.76	53.2	.68
54	10 x 35	2	0.17	36	1,110		2.53	53.9	.63
55	60 x 100	2	0.50	36	1,110	74	2.63	52.1	.62

Example V

Illinois coal ground to a minus 100 mesh was slurried with phosphoric acid, hypophosphorous acid, or a mixture of phosphoric and hypophosphorous acids. The excess

The invention having been described what we claim is:

1. The process of desulfurizing coal while producing a low sulfur char which comprises the steps of

(a) mixing crushed coal with an acid selected from the group consisting of orthophosphoric acid, polyphosphoric acids, phosphorous acids and mixtures thereof,

(b) removing excess acid from the coal whereby at least 0.25 weight percent acid based on weight of coal remains mixed with the crushed coal,

(c) heating the mixture in an inert atmosphere to an elevated temperature of between about 400 and 1300° F., and

(d) holding the mixture at the elevated temperature for at least 15 minutes whereby volatile sulfur compounds are removed from the coal while producing a char.

2. The process of claim **1** wherein the coal is mixed with an aqueous solution of an acid selected from the group consisting of orthophosphoric acid, polyphosphoric acids, phosphorous acids and mixtures thereof such that at least 1% by weight of the acid based on weight of coal remains in coal during the charring thereof.

3. The process of claim **2** wherein the heat up atmosphere is a flowing inert or mildly oxidizing atmosphere, the atmosphere during the time at temperature is a flowing reducing atmosphere and the cool down atmosphere is a flowing inert or mildly oxidizing atmosphere.

4. The process of claim **3** wherein the gas space velocity is between about 0.1 and 1.0.

5. The process of claim **4** wherein the mixture is heated to a temperature between about 900 and 1200° F. for at least 30 minutes.

6. The process of claim 1 wherein the acid is a mixture of H_3PO_4 and H_3PO_2.

7. The process of claim 1 wherein the crushed coal is between about 10 and about 100 mesh U.S. Sieve Series.

8. The method of desulfurizing high sulfur containing coals comprising the steps of:

(a) crushing coal to a size between about 100 and 10 mesh U.S. Sieve Series,

(b) slurrying the crushed coal with an aqueous solution of an acid selected from the group consisting of orthophosphoric acid, polyphosphoric acids, phosphorous acids and mixtures thereof,

(c) removing any excess acid solution from the coal-acid mixture such that at least about 1% by weight of the acid based on the weight of coal remains in the coal,

(d) heating the coal-acid mixture during a heat up period to a charring temperature between about 900 and 1200° F. in a flowing inert or mildly oxidizing atmosphere to initiate the charring of the coal,

(e) introducing a flowing reducing atmosphere to the coal-acid mixture while maintaining the charring temperature for at least about 15 minutes to produce a char and to remove the volatile sulfur compounds formed, and

(f) cooling the char to ambient temperature in a flowing inert or mildly oxidizing atmosphere.

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NORMAN YUDKOFF, Primary Examiner

H. H. BERNSTEIN, Assistant Examiner

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