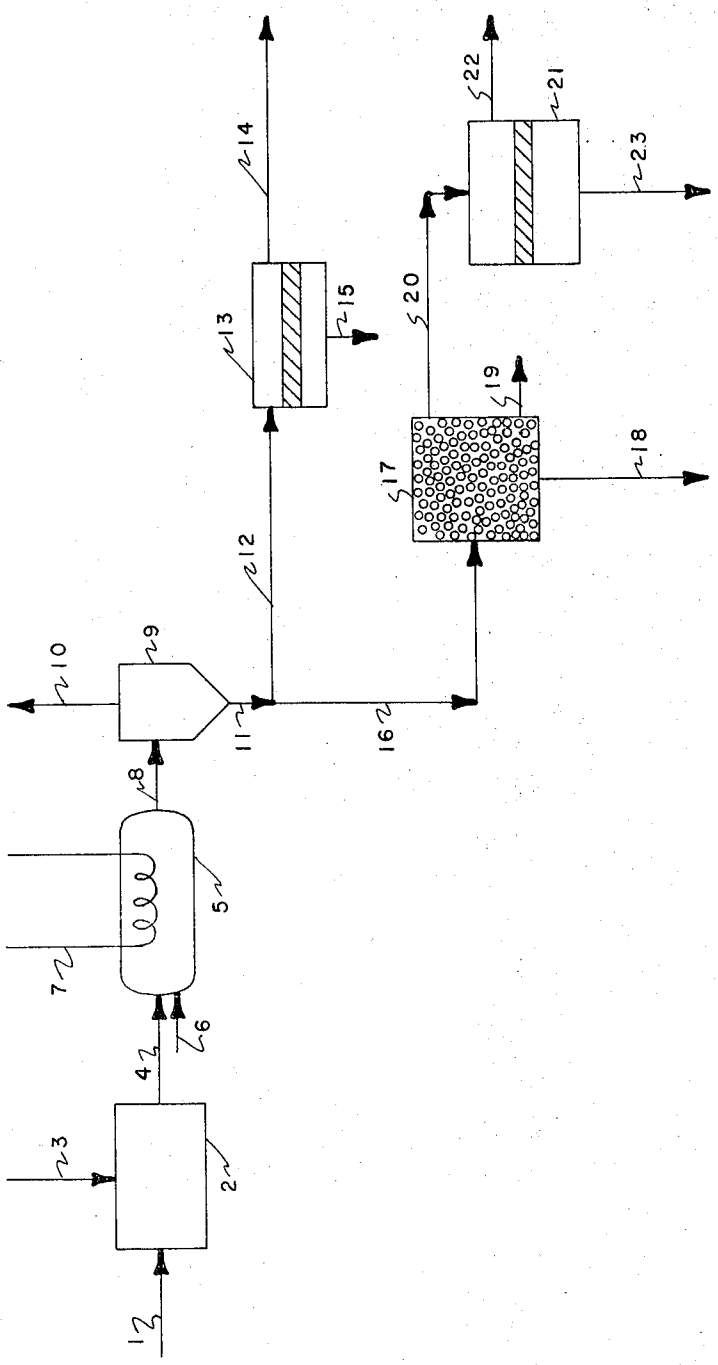
July 16, 1974 T. J. DILLON ET AL 3,824,084

PRODUCTION OF LOW SULFUR COAL

Filed Oct. 10, 1972



United States Patent Office 3,824,084 Patented July 16, 1974

3,824,084

PRODUCTION OF LOW SULFUR COAL

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Filed Oct. 10, 1972, Ser. No. 296,055
Int. Cl. C10l 9/00
U.S. Cl. 44—1 R 12 Claims

ABSTRACT OF THE DISCLOSURE

Coal containing pyritic sulfur is processed at elevated temperature and pressure with water and air to convert the pyritic sulfur to water-soluble ferrous and ferric sulfate. The resulting slurry is filtered to produce a coal product of diminished sulfur content which may be burned without causing air pollution due to sulfur dioxide emission.

BACKGROUND OF THE INVENTION

Field of the Invention

The invention relates to the treatment of coal to remove pyritic sulfur, so that the resultant coal product of low sulfur content may be burned in steam power plants and the like without causing appreciable air pollution due to sulfur dioxide emission in the flue gas.

Description of the Prior Art

The problem of air pollution due to the emission of sulfur dioxide when sulfur-containing fuels are burned has received increasing attention in recent years. Numerous proposals and schemes have been advanced for the removal of the sulfur dioxide from the flue gas generated when the fuel is burned, especially by scrubbing the flue gas with an aqueous alkaline solution or slurry, however, the alternative expedient of treating the fuel prior to combustion so as to remove the sulfur has received less attention. Prior art relative to the treating of coal includes U.S. Pats. Nos. 3,640,016; 3,632,479; 3,261,559; 2,346,151; 1,781,102 and 1,702,899. A typical process for the removal of sulfur from crude oil or petroleum fractions is catalytic hydrodesulfurization as described in U.S. Pat. No. 3,380,910, in which the sulfur-bearing oil fraction is treated with hydrogen in the presence of a suitable catalyst so as to evolve hydrogen sulfide and produce a sulfur-depleted oil phase. The treatment of pyrites etc. is described in U.S. Pat. Nos. 3,520,957 and 2,537,842.

SUMARY OF THE INVENTION

The present invention, the pyritic sulfur content of coal is effectively reduced or eliminated by reaction with water and air at elevated pressure and temperature. The invention is generally applicable to any type of coal, and within the context of the present invention it will be understood that the term "coal" refers to any type of solid carbonaceous fuel, such as anthracite coal, bituminous coal, sub-bituminous coal, lignite, peat, petroleum coke, etc., and the term "pyritic sulfur" refers to sulfur bound in chemical combination with iron within the coal, in the form of iron pyrites which is generally designated by the formula FeSx, where x may be any whole number or fraction from about 0.5 to about 4.

The coal containing pyritic sulfur is initially ground to a fine particle size in the presence of water, so as to produce a coal-water slurry containing discrete particles of finely divided coal. The slurry is pumped to an autoclave where it is heated and pressurized with air. The typical reaction equations which take place in the presence

of air and water at elevated temperature and pressure are as follows:

(1) $FeS_2+H_2O+7/2O_2 \rightarrow FeSO_4+H_2SO_4$

(2) $2FeSO_4+H_2SO_4+1/2\,O_2 \rightarrow Fe_2(SO_4)^3+H_2O$

The ferrous and feric sulfates formed are water soluble and are separated from the coal by filtration of the treated slurry, yielding a solid low sulfur coal product and a liquid tailing containing dissolved ferrous and ferric sulfate. Any elemental sulfur contained in the original coal is melted during the elevated temperature processing and is also discarded with the liquid tailings when filtration is made at temperatures above the freeze point of the sulfur.

Since the solubility of ferric sulfate decreases with increasing temperature, some of the iron pyrites may be converted to insoluble basic ferric sulfate. When this compound is formed, as an alternative embodiment of the invention, flotation and filtration following autoclaving yields the low sulfur coal. The ferrous and ferric sulfates are natural depressants for any remaining iron pyrites. Both depressants are active in acid mediums, so flotation of the autoclave effluent readily separates solid basic ferric sulfate from an overflow slurry of coal particles which is filtered to yield the low sulfur coal.

The advantage of the invention is that a low sulfur coal product is produced by inexpensive processing using readily available air and water. The system does not use a strong oxidizing agent to remove sulfur. It manufactures its own depressive agent in the event that a final flotation purification step is required or desired. The high cost of sulfur dioxide removal systems in exhaust stacks has imposed a demand for low sulfur content coal. Since most of this country's coal reserves are of the relatively high sulfur content bituminous type, the obvious solution both to problems of environmental protection and use of natural resources is the removal of sulfur compounds before such coals are burned. The need for new coal has become imperative due to government legislation and the proposed assessment of $0.22 to $0.33/kilogram of sulfur emitted into the air.

It is an object of the present invention to provide an improved process for the removal of pyritic sulfur from coal.

Another object is to remove pyritic sulfur from coal using inexpensive and readily available reactants.

A further object is to produce a low sulfur coal product in an improved manner.

An additional object is to prevent air pollution due to sulfur dioxide emission when coal is burned.

Still another object is to convert pyritic sulfur in coal to water-soluble ferrous sulfate and ferric sulfate by reaction with water and air at elevated pressure and temperature.

These and other objects and advantages of the present invention will become evident from the description which follows.

DESCRIPTION OF THE DRAWING AND PREFERRED EMBODIMENTS

Referring now to the drawing, a flowsheet showing alternative embodiments of the invention is presented. Coal stream **1** is derived from any suitable coal source or deposit from which coal may be mined by underground or strip mining methods. In this preferred embodiment of the invention, stream **1** consists of coarse lumps of bituminous coal containing in the range of about 1% to 5% pyritic sulfur by weight. Stream **1** is passed into the grinding device or apparatus **2**, which is any suitable device for reducing solid particulate matter to a finely divided state, such as a ball mill, a rod mill

or a hammer mill, water stream 3 is concomitantly passed into unit 2, and wet grinding of the coal particles to finely divided particles having a particle size distribution typically in the range of 10 mesh to 100 mesh takes place in unit 2. The mass flow rate of stream 3 is generally regulated to be about 20% to 80% of the mass flow rate of stream 1, so that an aqueous coal slurry stream 4 containing finely divided coal particles dispersed in an aqueous medium is discharged from unit 2. The processing of the coal in unit 2 serves to free elemental sulfur and trapped or bound iron pyrites.

Stream 4 is pumped into high pressure autoclave or reactor 5, which may be any suitable container or vessel capable of containing the process stream at high pressure for a suitable retention time, so that the desired reactions described supra may take place. Unit 5 may be provided with suitable internal baffles agitators or stirrers or the like to attain uniform dispersion of air or other oxygen-containing gas into the aqueous liquid slurry phase. Air stream 6 is concomitantly passed into unit 5, and sufficient air is pumped into unit 5 at elevated pressure so as to maintain an elevated pressure level typically in the range of 2 kg./sq. cm. to 50 kg./sq. cm. within unit 5. As the mixture of air and aqueous coal slurry proceeds through unit 5, the mixture is heated to an elevated temperature typically in the range of 90° C. to 200° C. by the provision of heating coil 7 within unit 5. Steam or other suitable hot heat exchange fluid is circulated through coil 7 to provide heating of the mixture within unit 5. The reaction mixture is typically retained within unit 5 for a time interval in the range of about 10 minutes to 100 minutes, and at least a porton of the pyritic sulfur present in oxidized in situ to ferrous sulfate and ferric sulfate, which concomitantly dissolve in the aqueous liquid phase. In most instances, a major portion of up to 90% or more of the pyritic sulfur is converted to water-soluble sulfate compounds in unit 5, however, in some instances, depending on the characteristics of the original minerals and pyritic sulfur present in the original coal feed stream 1, as well as specific operating parameters in a particular installation, some of the iron pyrites may be converted to solid basic ferric sulfate within unit 5.

In any case, a process effluent stream 8 is discharged from unit 5. Stream 8 now contains a solid phase which in most instances consists essentially of coal particles of diminished sulfur content, a liquid phase consisting essentially of an aqueous solution containing dissolved ferrous sulfate, ferric sulfate and molten sulfur, and a gaseous phase consisting of oxygen-depleted air. Stream 8 is preferably initially passed into gas-liquid separator 9, which is a baffled or cyclonic means or device for separating the gaseous phase of stream 8 from the liquid slurry phase. The separated gaseous phase is discharged from unit 9 via stream 10, and a substantially gas-free slurry stream 11 is removed from the lower portion of unit 9. Stream 11 may now be processed by alternate procedures, depending on whether stream 11 contains a substantial proportion of solid basic ferric sulfate. In most instances stream 11 will be substantially devoid of solid basic ferric sulfate, and in this case stream 11 is passed via stream 12 to filter 13, from which a solid phase stream 14 consisting of a finely divided low sulfur coal product is passed to product utilization, which will generally consist of the combustion of stream 14 in a steam boiler or furnace or the like. The separated aqueous liquid phase stream 15 is also removed from unit 13. Stream 15 is a liquid tailings consisting essentially of an aqueous solution containing dissolved ferrous sulfate and ferric sulfate. Stream 15 may be passed to suitable waste disposal, or stream 15 may be processed to recover ferrous sulfate and/or ferric sulfate for product sales or utilization, by evaporative crystallization or the like.

In instances when stream 11 contains an appreciable proportion of solid basic ferric sulfate, stream 11 is processed in an alternative embodiment of the invention to initially remove the solid basic ferric sulfate by flotation. In this procedure, the dissolved ferrous sulfate and ferric sulfate act as in situ natural depressants and aid in the flotation separation process. Stream 11 in this case flows via stream 16 to flotation vessel 17. A flotation-inducing stream 18 which may consist of air or water or other fluid is introduced into the lower portion of vessel 17 and rises through the fluid slurry body maintained in vessel 17, thereby selectively moving coal particles upwards while allowing the particles of solid basic ferric sulfate to remain in the lower portion of vessel 17. A stream 19 consisting essentially of an aqueous slurry of solid basic ferric sulfate is removed from the lower portion of unit 17. Stream 19 may be passed to solids tailings disposal, or stream 19 may be further processed as desired to produce a salable sulfate product.

An aqueous coal slurry stream 20 is removed from the upper portion of unit 17. Stream 20 contains product solid low sulfur coal particles and an aqueous liquid phase containing dissolved ferrous sulfate and ferric sulfate. Stream 20 is now processed in a manner similar to the processing of stream 12 described supra. Stream 20 is passed into solid-liquid separation filter 21, from which a low sulfur solid coal product is removed via stream 22, which is passed to product utilization. A liquid tailings solution stream 23 is also removed from unit 21, and stream 23 may be passed to disposal or utilization in a manner similar to stream 15 described supra.

Numerous alternatives within the scope of the present invention will occur to those skilled in the art. Process water may be alternatively or additionally added to stream 1 prior to unit 2. Stream 6 may consist of any suitable oxygen-containing gas, such a substantially pure oxygen, oxygen-enriched air or the like. Streams 4 and/or 6 may be initially heated prior to entry into unit 5. Stream 8 may be initially passed through a pressure reducing valve prior to the passage of stream 8 into unit 9. Units 13 and/or 21 may alternatively consist of centrifuges or other known devices for separating a solid phase from a liquid phase, and thus the "filtering" of slurry streams 12 and/or 20 will be understood to encompass any suitable solid-liquid separation means or device. Similarly, the term "flotation" will be understood to encompass heavy media separation techniques or other comparable procedures for separating two solid phases of differing densities or characteristics. In this respect, known flotation agents or reagents such as an oil may be added to stream 16 in suitable instances to enhance the processing in unit 17 and attain better separation of basic solid ferric sulfate particles from the product low sulfur coal particles.

An example of application of the process of the present invention will now be described.

EXAMPLE

The autoclave charge was 200 grams of coal and 467 grams of water. The coal was ground to 100 mesh and initial analysis was 2.55% total sulfur, 0.94% organic sulfur, and 28.6% volatiles. The autoclave conditions were 175° C., 42.2 kg./sq. cm. pressure, provided via air injection. Reaction time was 10 minutes and agitation at 600 r.p.m. was provided. The autoclave contents were blown through a preheated filter at the end of the run. The coal was then dried and analyzed for sulfur. Total sulfur by Eschka method was 0.48%.

What is claimed is:

1. A process for the removal of pyritic sulfur from coal which comprises adding water to coal particles, said coal particles containing pyritic sulfur, grinding said coal particles in the presence of said water, whereby an aqueous slurry containing finely divided coal particles is produced, heating said aqueous slurry to a temperature in the range of 90° C. to 200° C. at elevated pressure in the range of 2 kg./sq. cm. to 50 kg./sq. cm. and in the presence of a gas containing free oxygen for a time interval in the

range of about 10 minutes to 100 minutes, whereby at least a portion of said pyritic sulfur is oxidized to ferrous sulfate and ferric sulfate, said ferrous sulfate and ferric sulfate being dissolved in situ in said water, and filtering the resulting slurry, whereby a finely divided coal product of reduced pyritic sulfur content is produced.

2. The process of claim 1, in which said coal particles are ground to an average particle size in the range of 10 mesh to 100 mesh.

3. The process of claim 1, in which said gas is air.

4. The process of claim 1, in which a major portion of said pyritic sulfur is oxidized to ferrous sulfate and ferric sulfate.

5. The process of claim 1, in which said coal is a bituminous coal.

6. The process of claim 1, in which said water is added to said coal particles during the grinding of said coal particles.

7. A process for the removal of pyritic sulfur from coal which comprises adding water to coal particles, said coal particles containing pyritic sulfur, grinding said coal particles in the presence of said water, whereby an aqueous slurry containing finely divided coal particles is produced, heating said aqueous slurry to a temperature in the range of 90° C. to 200° C. at elevated pressure in the range of 2 kg./sq. cm. to 50 kg./sq. cm. and in the presence of a gas containing free oxygen for a time interval in the range of about 10 minutes to 100 minutes, whereby at least a portion of said pyritic sulfur is oxidized to ferrous sulfate, ferric sulfate and solid basic ferric sulfate, said ferrous sulfate and ferric sulfate being dissolved in situ in said water, said solid basic ferric sulfate being substantially insoluble in the resulting aqueous liquid phase, separating an aqueous coal slurry containing dissolved ferrous sulfate and ferric sulfate from said basic ferric sulfate by flotation, and filtering said separated aqueous coal slurry whereby a finely divided coal product of reduced pyritic sulfur content is produced.

8. The process of claim 7, in which said coal particles are ground to an average particle size in the range of 10 mesh to 100 mesh.

9. The process of claim 7, in which said gas is air.

10. The process of claim 7, in which a major portion of said pyritic sulfur is oxidized to ferrous sulfate and ferric sulfate.

11. The process of claim 7, in which said coal is a bituminous coal.

12. The process of claim 7, in which said water is added to said coal particles during the grinding of said coal particles.

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U.S. Cl. X.R.

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