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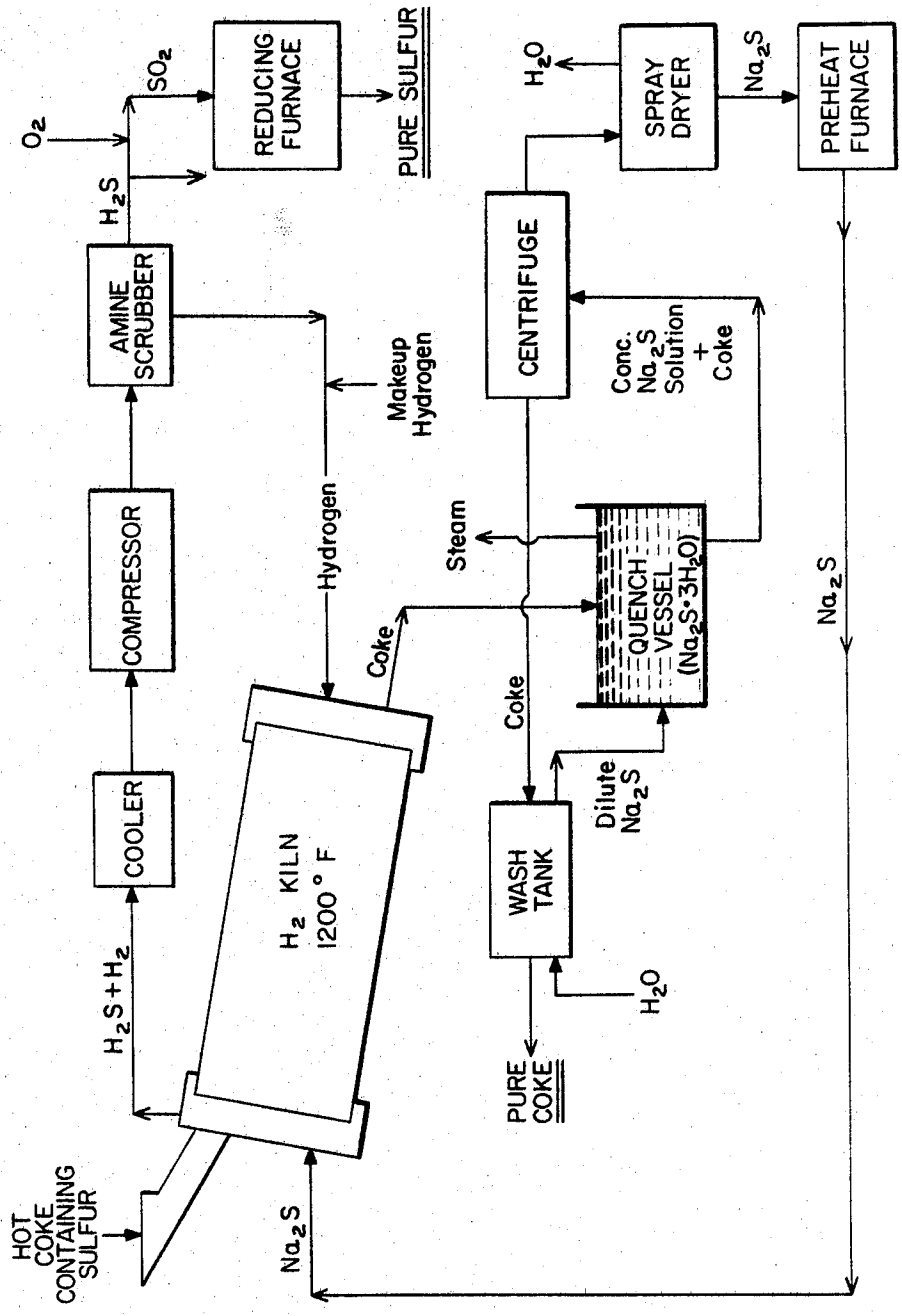

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DESULFURIZATION OF COKE

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ABSTRACT OF THE DISCLOSURE

A complete process is described for the desulfurization of carbonaceous solids, in particular, fluid coke derived from petroleum residuums. The process involves mixing of the raw coke with a finely divided alkali metal sulfide such as sodium sulfide and passing hydrogen gas through the mixture at moderate temperatures. Sulfur is removed from the coke primarily as hydrogen sulfide, is separated from the unreacted hydrogen and recovered by conventional means. The reacted coke and sodium sulfide are separated by water washing; the sodium sulfide being water soluble. Spray drying returns the sodium sulfide to its original condition so that it may be recycled.

This invention relates to a method for desulfurizing carbonaceous solids. The desulfurized solids may then be used as any low sulfur carbonaceous material; that is, a fuel, electrodes, etc. This process also provides for the recovery of the sulfur removed. The process development work has been carried out using fluid petroleum coke, a product produced in large tonnage by oil refineries.

Hydrogen is well known for its properties as a partially effective desulfurizing agent of coke; it reacts with part of the sulfur content of the coke to produce hydrogen sulfide gas. It is also known that the effectiveness of hydrogen as a desulfurizing agent is increased if the coke is subjected to a pre-oxidation treatment with an oxygen-containing gas such as air, prior to treatment with hydrogen. Reactions of this type have been carried out with the coke fluidized by the gas that is used for treatment, i.e., by conducting the treating gas upwardly through a bed of the coke at such a velocity as to maintain the entire bed in a flowable condition.

The patent to Johnson et al. No. 3,009,781 discloses a process wherein a fluidized bed of coke is maintained, the coke is treated with hydrogen gas, and an electric current is passed through the bed in a manner to create temperatures of approximately 650 to 800° C., or approximately 1200 to 1500° F.

The patent to Johnson et al. also discloses that the effectiveness of hydrogen as a desulfurizing agent for coke which has not been pre-oxidized is increased if, in a separate step, the coke is preliminarily impregnated with a water solution of an alkali metal compound such as potassium or sodium hydroxide or carbonate. Calcium hydroxide and calcium oxide are less effective. According to the Johnson et al. patent, the coke is treated with aqueous solutions of these alkali metal hydroxides or carbonates in amounts to provide approximately 2–8% by weight of the alkali metal hydroxide or carbonate, based upon the weight of the coke. Johnson et al. also disclose that the effectiveness of hydrogen is still further increased if both pre-oxidation and alkali treatments are applied to the coke.

While the Johnson et al. patent does not explicitly state so, the sodium must be removed and recovered from the coke after reaction. This is accomplished by a solution procedure using appropriate solvents such as water. The sodium is recovered as sodium sulfide. Thus, at least

part, if not all of the sulfur removal is through the conversion of the sodium hydroxide to sodium sulfide.

It has now been discovered that excellent desulfurization of coke at a much reduced cost can be achieved by converting the sulfur primarily into hydrogen sulfide, by continuously adding to a reactor, along with the coke, a minimum amount of finely subdivided particles of sodium sulfide. The desulfurization reaction is conducted by intimate contact with hydrogen in a continuously operating kiln at temperatures in the range of 1100 to 1600° F., preferably approximately 1200°–1300° F. The effectiveness of solid sodium sulfide is considered wholly unexpected, because as mentioned above the reactions involved in converting the complicated sulfur compounds in the coke have been found to produce sodium sulfide as an end product, which would lead one to believe that the introduction of further sulfide would suppress rather than enhance the decomposition of these sulfur compounds.

Reference is hereby made to the drawing, which is a simplified flow diagram illustrating one specific manner in which the invention can be carried out.

Referring to the drawing, hot coke which contains sulfur is fed into the feed hopper of the kiln, which is maintained at approximately 1200° F. According to this invention, solid sodium sulfide is introduced continuously at the feed end of the kiln. Hydrogen is fed at the opposite end of the kiln, and reacts with the sulfur contained in the coke producing hydrogen sulfide plus excess hydrogen at the exit of the kiln. The treated coke passes out the lower end of the kiln and is dropped into a quench vessel containing a concentrated solution of sodium sulfide.

The mixture of gases at the stack is cooled, compressed and subjected to amine scrubbing which recovers hydrogen sulfide. The hydrogen sulfide can be converted to sulfuric acid, elemental sulfur or other sulfur containing compounds by known methods.

The coke from the kiln passes, as stated, into the quench vessel where it is intimately mixed with a concentrated solution of sodium sulfide. This results in a solution of sodium sulfide from the coke, and after centrifuging the coke is then subjected to further water washing and emerges as a desulfurized coke product. The sodium sulfide solution from the centrifuge is passed to a spray dryer, and the dry solid sodium sulfide is reheated and reintroduced at the feed end of the kiln along with further sulfur-containing coke.

Equivalent materials may be introduced as substitutes for, or additives to, the sodium sulfide which enhances the desulfurization reaction. Such equivalents include sodium hydrosulfide (NaHS) and sodium thiosulfate ($Na_2S_2O_3$). Further, ingredients may be introduced which react under the conditions existing in the desulfurizing kiln, to produce compounds such as sodium sulfide. For example, under operating conditions of the kiln at 1200° F. in a hydrogen atmosphere, sodium hydroxide or solid sodium carbonate react with the sulfur compounds initially present in the coke to produce compounds such as sodium sulfide, and also react with liberated hydrogen sulfide, thus enhancing the desulfurization reaction within the kiln. Therefore, even though the process operates in an excellent manner with sodium sulfide alone, it is preferred in some cases to provide sodium hydroxide or sodium carbonate as a solid make-up.

The relative proportions of sodium sulfide to coke in accordance with this invention are of importance. It is preferable to employ approximately 0.15 ton of sodium sulfide per ton of hot coke, or to employ a range of from about 0.01 to 0.30 ton of sodium sulfide per ton of coke. Similar proportions apply to the sodium sulfide equivalents referred to above.

If desired, all or part of the sodium sulfide in the quench liquor may be converted to sodium carbonate by bubbling carbon dioxide through the quench liquor and freeing H_2S for recovery.

One of the most common uses of fluid petroleum coke is as a fuel, but the sulfur content of large tonnages of fluid coke ranges from 3–7% by weight or more, and the combustion of coke produces sulfur dioxide and other sulfur-containing compounds that escape to the atmosphere and create air pollution problems. With the recently increased emphasis on controlling air contamination, fluid coke and all other fuels that contain appreciable amounts of sulfur are subject to restricted use or even total replacement unless a means can be developed to minimize the evolution of sulfur oxides from facilities where this coke is burned. Accordingly, the process of this invention is highly desirable for this purpose.

The following examples illustrate specific ways in which the invention has been carried out:

Example 1

Fluid coke containing 6.0% sulfur was desulfurized with hydrogen gas only, under the following conditions:

Time ____ hour__	1
Temperature ____ ° F__	1180
Hydrogen flow rate ____ [1]	1100

[1] Volume of H_2/volume of coke/hour.

Analysis of the coke after the reaction showed 5.2% sulfur remained, giving a net desulfurization of 13%.

Example 2

Another feed of the same fluid coke used in Example 1 was reacted in a similar manner but with the addition of 0.12 pound of sodium sulfide per pound of coke. The sodium sulfide was technical grade $Na_2S \cdot 3H_2O$ with the water being evaporated before turning on the hydrogen flow. Operating conditions were:

Time ____ hour__	1
Temperature ____ ° F__	1200
Hydrogen flow rate ____ [1]	1000

[1] Volume of H_2/volume of coke/hour.

Hydrogen sulfide was produced at the rate of 760 s.c.f. per ton of coke fed. After the reaction the coke was cooled, washed with water, dried and analyzed for sulfur. The sulfur content of the coke was 3.20% indicating 47% desulfurization.

Example 3

Another feed of the same coke as used in Example 1 was reacted with hydrogen and spray dried sodium sulfide. In this case the $Na_2S \cdot 3H_2O$ had been spray dried with hot air, removing most of the water of hydration. Desulfurization conditions were as follows:

Na_2S/coke ratio ____	0.12
Temperature ____ ° F__	1220
Time ____ hours__	1.5
Hydrogen flow rate ____ [1]	1000

[1] Volume of H_2/volume of coke/hour.

After cooling and water washing, the coke analyzed 2.4% sulfur; i.e., 60% desulfurization.

Desulfurization was accomplished by the removal of hydrogen sulfide, not the formation of a sodium compound containing more sulfur than the sodium sulfide feed. In fact, the sodium and sulfur in the wash solution were present in a ratio of 2.5, significantly higher than the 2.1 ratio measured in the spray dried feed. This indicates that some of the sulfur was actually removed from the sodium sulfide even though literature references state that sodium sulfide is stable at 1200° F. in a hydrogen atmosphere.

Example 4

A different fluid coke, containing 3.55% sulfur, was reacted with sodium sulfide which contained approximately 4% water. The operating conditions were:

Na_2S/coke ratio ____	0.15
Temperature ____ ° F__	1250
Hydrogen flow rate ____ [1]	1650

[1] Volume of H_2/volume of coke/hour.

Samples were removed from the reactor at 30 minute intervals, washed, dried, and analyzed with the following results:

Time (min.)	Residual sulfur	Percent desulfurization
30	1.7	52
60	1.4	61
90	1.2	66
120	1.0	72

A typical material balance on the process shown in the drawing is as follows:

Example 5

Coke to kiln (6.6% S) ____ #/min__	2500
Na_2S to kiln ____ #/min__	375
H_2S from amine scrubber ____ s.c.f./min__	1360
Recycle gas from amine scrubber ____ s.c.f./min__	30,000
Kiln residence time ____ hours__	2
Coke to quench ____ #/min__	2605
Na_2S solution to spray dryer ($Na_2S \cdot 3H_2O$) #/min__	591
Flue gas+H_2O from spray dryer ____ #/min__	236
Na_2S from spray dryer ____ #/min__	355
Makeup Na_2S or Na_2CO_3 ____ #/min__	20
Product coke (2.0% S) ____ #/min__	2300

While desulfurization techniques with gaseous agents such as hydrogen, nitrogen, carbon dioxide, steam and even sulfur dioxide have been proposed, and although some of those processes do achieve substantial desulfurization, none of them has the efficiency or low cost of the process according to this invention, wherein it has been discovered surprisingly that an alkali metal sulfide has a strong desulfurization value.

There are several major economic advantages to the process described here over previous processes. First, the sodium sulfide can be heated separately from the coke and added to the kiln as separate particles. Since impregnation of the sodium sulfide into the coke is not necessary, advantages can be taken of the fact that fluid coke is available from fluid cokers at a temperature of 1100–1150° F. A slight additional burn of this hot coke raises it to desulfurization temperature with only a small yield loss. Pre-calcination, pre-oxidation or other coke pretreatments are unnecessary. A second major advantage is that the sodium sulfide can be recycled directly, eliminating expensive conversion to sodium carbonate or sodium hydroxide.

Although satisfactory desulfurization occurs within a range of about 1000° F. to about 1400° F., the temperature has an influence upon both the hydrogen consumption rate and the amount of sodium sulfide left with the coke following the treatment. As the processing temperature increases, the hydrogen consumption decreases and the residual sodium left on the coke after washing increases, and vice versa. The results of desulfurizing several different cokes at various temperature within this range has established that a temperature of approximately 1200° F. to 1300° F. is highly preferred since it reduces the sulfur content to an acceptable limit without using an excessive amount of hydrogen or leaving too great a quantity of sodium on the coke.

Unlike many of the known processes for desulfurization, this process is preferably carried out at atmospheric pressure; thus there is no need for pressure equipment

which is usually costly. The time required to desulfurize the coke by the process according to this invention varies with the original sulfur content of the coke and the temperature of the reaction. In general, a period of approximately ten minutes to three hours in the kiln is sufficient. Under optimum conditions, adequate desulfurization of a coke containing approximately 6% sulfur can usually be achieved within one to two hours at a temperature of approximately 1200° F.

It is a great advantage that along with the hot coke the sodium sulfide may be introduced into the kiln in solid form to catalyze the desulfurization reaction. Other processes using a solution sprayed into the kiln by continuous pumping, have the disadvantage of quenching the kiln and imposing a very substantial heat burden.

It is to be emphasized that no pre-treatment of the raw coke such as by oxidation or calcination is required before desulfurizing it according to the process of this invention. Moreover, contrary to prior processes, it is unnecessary to pre-cool the hot coke, impregnate it with a treating solution, and then reheat it for introduction into the desulfurizing process. Thus, all of the expenses of time, equipment, heat and the like associated with these pre-treatments are eliminated.

Although the flow rates of hydrogen used in the process according to this invention can be varied within wide limits, it has been found that a rate of approximately 300 volumes of hydrogen per volume of coke per hour produces excellent results.

The following is claimed:

1. A method of separating sulfur from petroleum coke which comprises intimately mingling a compound selected from the group consisting of sodium sulfide, sodium sulfate, sodium hydrosulfide and sodium thiosulfate with said coke in an amount of about 0.01 to 0.30 ton per ton of said coke, heating to approximately 1100 to 1500° F. in a sweep of hydrogen- containing gas to remove most of the sulfur impurity as hydrogen sulfide, and recovering the desulfurized coke by solubilizing the sodium sulfide present in said coke.

2. The method defined in claim **1** wherein said compound is added in the solid state.

3. The method according to claim **1** wherein said compound is sodium sulfide.

4. The method according to claim **1** wherein said temperature is 1200–1300° F.

5. The method according to claim **1** wherein the flow rate of hydrogen is at least 300 volumes per hour per volume of coke.

6. The method according to claim **1** wherein the desulfurized coke is quenched in a strong solution of sodium sulfide, and wherein the sodium sulfide in the quench liquid is recovered by drying and is recycled to the feed end of the process.

7. The method defined in claim **6** further characterized by the fact that the coke is removed from the quench and washed with water, and the wash water is fed to the quench.

References Cited

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