Oct. 14, 1969 R. D. RIDLEY 3,472,624

DESULFURIZATION OF PARTICULATE COKE

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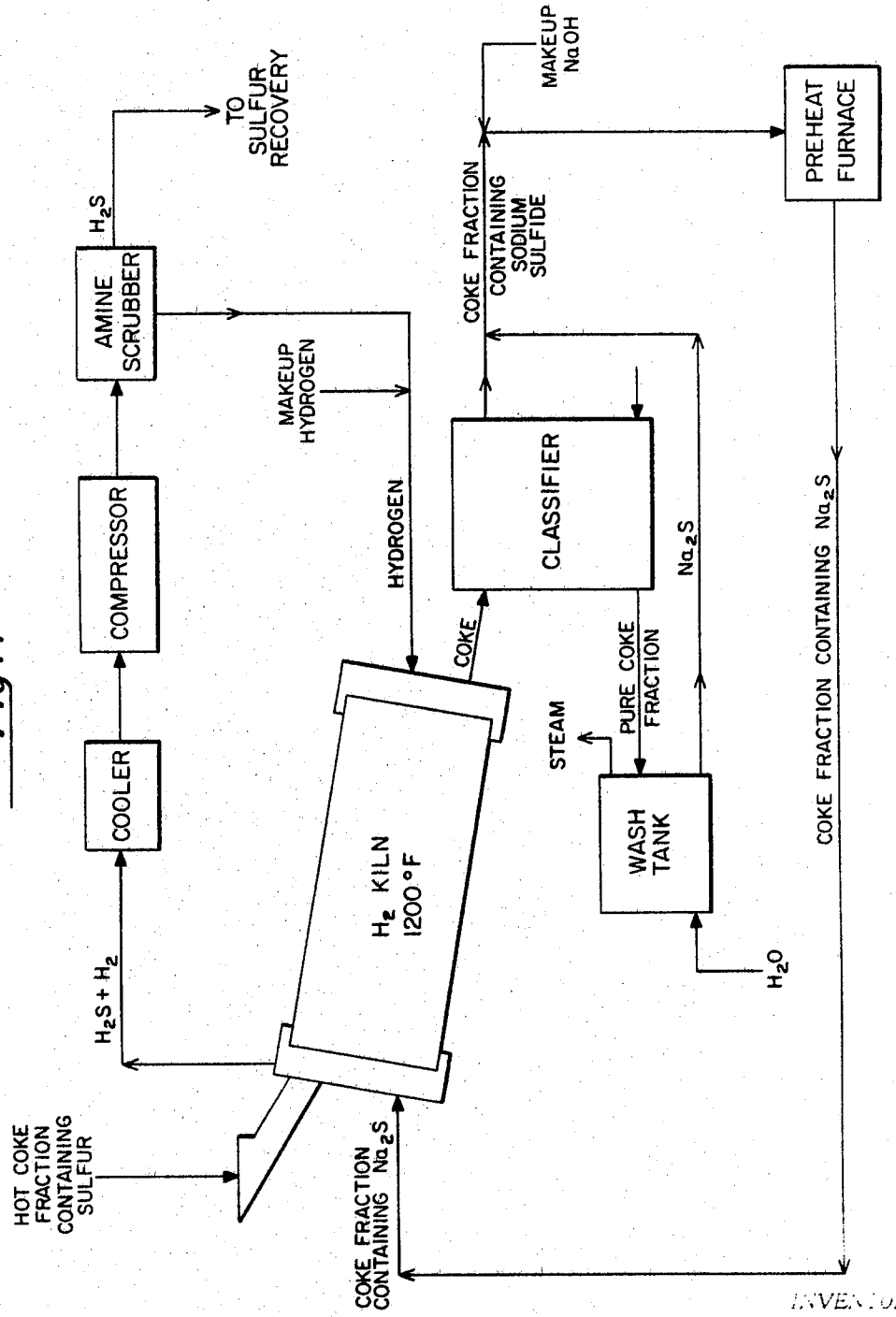

Fig. 1

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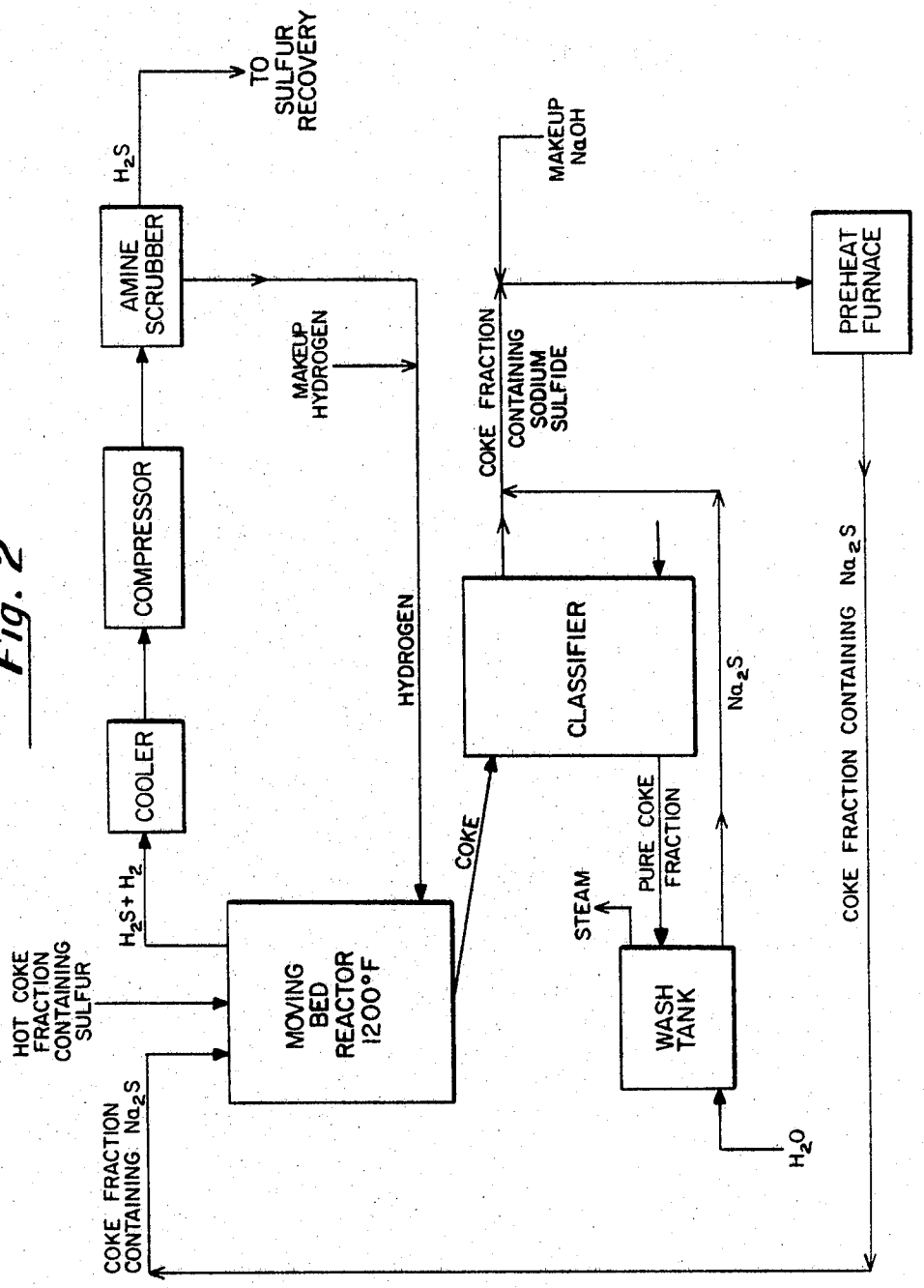
Fig. 2



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United States Patent Office 3,472,624 Patented Oct. 14, 1969

3,472,624

DESULFURIZATION OF PARTICULATE COKE

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Continuation-in-part of application Ser. No. 580,322, Sept. 19, 1966. This application Apr. 5, 1967, Ser. No. 628,733

Int. Cl. C01b *31/02;* C10b *57/12*

U.S. Cl. 23—209.9 4 Claims

ABSTRACT OF THE DISCLOSURE

Particulate coke is classified into at least two different particle size fractions, one of which fractions is then impregnated with sodium sulfide. The impregnated fraction and at least one unimpregnated fraction are combined and heated together in a hydrogen atmosphere at temperatures of 1100–1600° F., whereupon a reduction in the sulfur content of the unimpregnated fraction is effected. The desulfurized fraction is then recovered by classification, while the impregnated fraction may be recycled.

CROSS REFERENCE TO RELATED APPLICATION

The prior art is fully described in my pending application, Ser. No. 580,322, Sept. 19, 1966, the disclosure thereof being incorporated herein by reference and made a part hereof.

BACKGROUND OF THE INVENTION

Field of the invention

My pending application, hereinabove referred to, pertains to the discovery 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, while heating the reactor contents in a hydrogen atmosphere to temperatures in the range of from about 1100° F. to about 1600° F.

Description of the prior art

The prior art is fully described in my copending application Ser. No. 580,322, filed Sept. 19, 1966. The process of this invention provides for the more effective utilization of the desulfurization process of said pending application.

SUMMARY OF THE INVENTION

It has now been discovered that the desulfurization of coke and similar carbonaceous materials by the process including the steps of reacting the materials in the presence of sodium sulfide in a hydrogen atmosphere at temperatures in the range of from about 1100° F. to about 1600° F. may be accomplished more effectively if the sodium sulfide is presented for reaction as an impregnate on carbonaceous material itself, or as a reaction product of a sodium compound and a sulfur containing carbonaceous material. In some way, the use of other carbonaceous material as a carrier for the desulfurizing agent containing sodium provides for more effective desulfurization.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a flow diagram of one embodiment of the process of this invention.

FIG. 2 is a flow diagram of another embodiment of the process of this invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to FIG. 1, a hot coke fraction which contains sulfur is fed into the feed hopper of the kiln which is maintained at approximately 1200° F. According to the process of this invention, a different, preferably smaller particle size, fraction of hot coke which has been impregnated with 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 combined fractions of coke after being treated in the kiln pass out the lower end of the kiln into a classifier. A purified coke fraction is removed from the classifier and passed to a wash tank where residual sodium sulfide which has been transferred to it in the reactor is washed from such fraction and recycled into the process. The purified coke fraction is recovered from the wash tank. The fraction of coke separated in the classifier consisting predominantly of small coke particles embedded with sodium sulfide is recycled back to the kiln after reheating in the preheat furnace. Sodium sulfide resulting from the aforementioned wash of the larger particles and any required make-up sodium compound are blended back with the smaller coke fraction prior to reheating. A liquid-solids type blender may be used for this reblending. From the preheat furnace is taken the initial coke fraction impregnated with 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.

Referring to FIG. 2, there is shown a modified flow diagram in which embodiment the reactions between the coke fractions are carried out in a moving bed reactor instead of in the kiln of FIG. 1.

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 ($Na_2S_2O_3$). The amount of sulfur-bearing compound to be added should be within the range of about 0.01 ton to about 0.30 ton per ton of petroleum coke.

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.

Example I

A supply of fluid coke was screened to give a minus 60 plus 80 Tyler mesh fraction and a minus 150 plus 200 Tyler mesh fraction. Each fraction contained 6.0% by weight sulfur. Two hundred grams of the minus 150 plus 200 fraction were coated with 40 grams of sodium hydroxide as an aqueous solution, which was then dried, and the fraction rescreened to minus 150 plus 20 mesh. This coke fraction analyzed 8.69% Na. Two hundred grams of this sodium hydroxide impregnated minus 150 plus 200 mesh coke was mixed with 300 grams of the untreated minus 60 plus 80 mesh coke and reacted together

at 1200° F. for one hour with hydrogen gas fluidizing the mxiture. At the end of this time the combined fractions were rescreened and analyzed as follows:

Weight recovered	Minus 60 plus 80	Minus 150 plus 200
Wt. of sample recovered (g.)	281	169
Percent Sulfur	4.3	N.D.
Percent Sodium		6.81

N.D.—Not determined.

It was apparent that in this run, very little desulfurization of the minus 60 plus 80 particles occurred. Instead, most of the available sodium was converted to Na_2S utilizing the available sulfur in the smaller particles.

Example II

140 grams of once reacted minus 150 plus 200 mesh from Example I coke was mixed with 290 grams of unreacted minus 60 plus 80 mesh coke and the combined fractions reacted for 2 hours at 1200° F. in a bed fluidized by hydrogen gas. The combined fractions were again rescreened and analyzed. The minus 60 plus 80 mesh fraction was also washed to remove the sodium transferred to it during the reaction. The analysis were as follows:

Weight recovered	Minus 60 plus 80 before wash	Minus 60 plus 80 after water wash	Minus 150 plus 200
Wt. of sample recovered (g.)	260	N.W.	126
Percent S	2.7	1.86	N.D.
Percent Na	2.1		1.4
Percent desulfurization	55	69	

N.W.—Not weighed.
N.D.—Not determined.

The amount of sodium present in Example II would be equivalent to 0.056 pound of sodium sulfide per pound of fresh coke fed to the reactor. The ratio would be even lower on a total coke to the reactor basis. The remarkable discovery is that this small amount of sodium sulfide would accomplish almost 70% desulfurization. Reference to Example III in my application, Ser. No. 580,322 shows that almost three times as much sodium sulfide was required to obtain essentially the same percent desulfurization when the sodium sulfide was supplied as separate, finely divided particles. The economic advantages of this process improvement include the following:

(1) The separation of the different sized fractions may be carried out while the coke is still hot. The fraction being returned to the reactor will need only a small amount of additional heat.

(2) A much smaller amount of sodium sulfide must be removed from the desulfurized coke than in the prior method. This amount can be reblended with the recycle coke without the use of expensive spray drying.

Although satisfactory desulfurization occurs within a range of about 1100° F. to about 1600° F., the temperature has an influence upon both the hydrogen consumption rate and the amount of sodium sulfide left in the particles following 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 temperatures 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 10 minutes to 3 hours in the reactor is sufficient. Under optimum conditions, adequate desulfurization of a coke containing approximately 6% by weight sulfur can usually be achieved within 1 to 2 hours at a temperature of approximately 1200° F.

It is to be further 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.

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.

Having thus described my invention, I claim:

1. In a method of separating sulfur from petroleum coke including the step of (1) subjecting said coke to a temperature within the range of from about 1100° F. to about 1600° F. in the presence of hydrogen gas and an amount of compound selected from the class consisting of sodium sulfide, sodium hydrosulfide and sodium thiosulfate, within the range of from about 0.01 ton to about 0.30 ton of said compound per ton of coke, wherein the improvement comprises (2) presenting said compound in step (1) in the form of a particle size fraction of said coke impregnated with said compound, said impregnated particle size fraction capable of being mechanically separated by size from said coke which has not been impregnated with said compound.

2. The method in accordance with claim **1** wherein the compound is sodium sulfide.

3. The method in accordance with claim **1** wherein said temperature is in the range of from about 1200° F. to about 1300° F.

4. The method in accordance with claim **1** wherein the flow rate of hydrogen is at least 300 volumes per hour per volume of said coke.

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U.S. Cl. X.R.

23—181; 201—17, 31, 36, 42