

[54] **DESULFURIZING COKE WITH PHOSGENE OR A MIXTURE OF CARBON MONOXIDE AND CHLORINE**

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[56]

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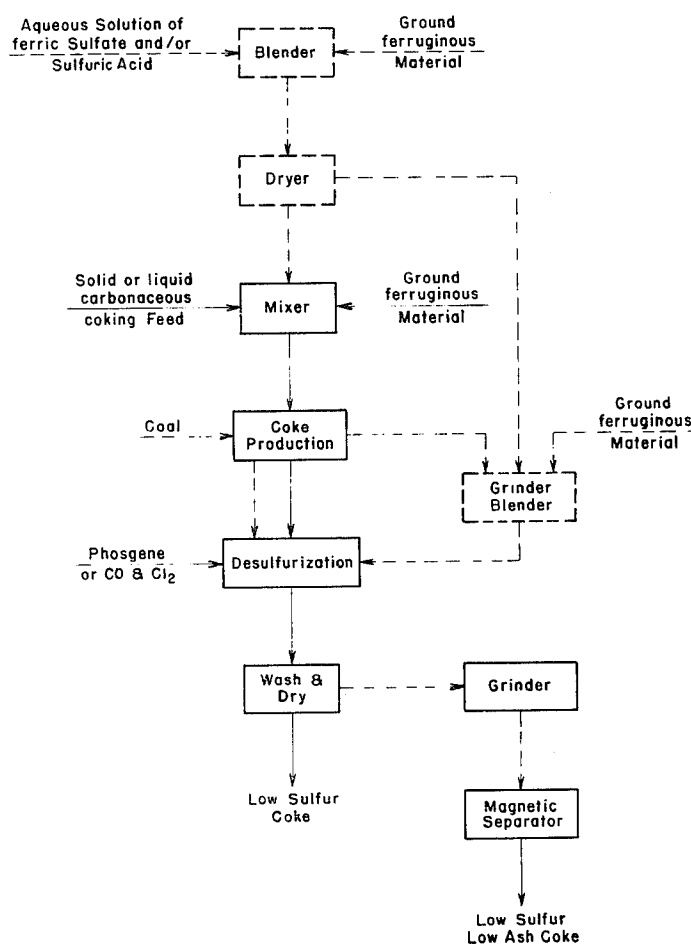
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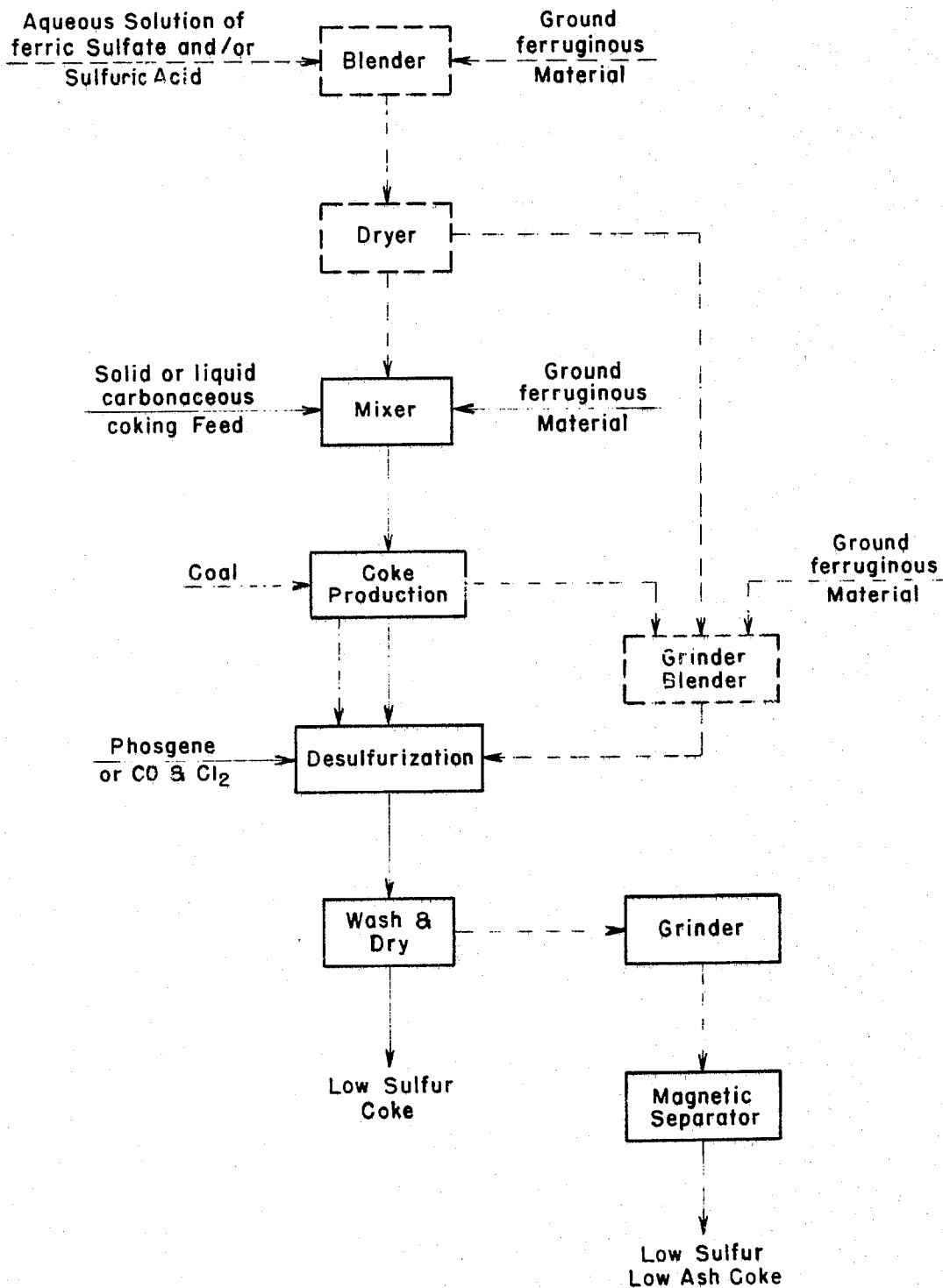
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## ABSTRACT

Coke is desulfurized by contacting coke with phosgene gas or a mixture of carbon monoxide and chlorine, at a temperature from 1200°–1800°F. to produce coke having a sulfur content of no greater than 0.85%. The coke may be admixed with a ferruginous material and/or ferric sulfate or sulfuric acid as a desulfurizing promoter.

**17 Claims, 1 Drawing Figure**





## DESULFURIZING COKE WITH PHOSGENE OR A MIXTURE OF CARBON MONOXIDE AND CHLORINE

This application is a continuation-in-part of application Ser. No. 309,470 filed on Nov. 24, 1972, and now abandoned.

This invention relates to the desulfurization of coke, and more particularly to a new and improved process for producing a coke having a sulfur content of less than 0.85%.

There has been proposed a wide variety of processes for producing desulfurized coke. In general, however, such processes are not effective for producing a desulfurized coke from a wide variety of feedstocks having various sulfur contents, including sulfur contents of 4 percent and greater, which would meet today's standards of a sulfur content of less than 0.85 percent, and preferably less than 0.5 percent.

Accordingly, an object of the present invention is to provide a process for providing desulfurized coke.

Another object of the present invention is to provide a desulfurized coke having a sulfur content of less than 0.5%.

A further object of this present invention is to provide a process capable of producing a desulfurized coke having a sulfur content of less than 0.5% which is prepared from feedstocks having both high and low sulfur contents.

These and other objects of the present invention should be more readily apparent from reading the following detailed description thereof with reference to the accompanying drawing wherein:

The drawing is a simplified schematic flow diagram illustrating processing steps of the present invention.

In accordance with the present invention, there is provided a process for desulfurizing coke wherein the coke is contacted with a desulfurizing gas, with or without the presence of other additives, at a temperature from about 1200°F. to about 1800°F. for a time sufficient to produce a coke having a sulfur content of no greater than 0.85%, and preferably no greater than 0.5%.

The desulfurizing gas is either a mixture of carbon monoxide and chlorine or phosgene, and generally also includes a diluent gas, such as nitrogen, in order to minimize the concentration of phosgene (phosgene is also generated when using a mixture of carbon monoxide and chlorine). It is to be understood, however, that a diluent gas need not be present although the use of a diluent is preferred. Although the desulfurization is effected under reducing conditions, oxygen can also be present in the gas. In employing a mixture of carbon monoxide and chlorine, the relative proportions of the two materials can vary over a wide range, in that it is believed that the desulfurization is effected by in situ generation of phosgene. As should be apparent, it is most economic to employ the carbon monoxide and chlorine in amounts approximating equimolar amounts. Typically, the ratio of one of the two components to the other ranges from about 0.5:1 to 1.5:1. As should be apparent, however, the relative proportions can be outside such a typical range in that in situ phosgene generation can occur outside such ranges, although such an operation is not preferred.

In the case where the coke which is to be desulfurized is produced from a petroleum feedstock, the coke is

mixed with a desulfurizing amount of a ferruginous material (iron, oxide of iron or mixtures thereof), as a desulfurizing additive. In the case where the coke is derived from coal containing pyrites, i.e., pyrites is present in an amount of at least 0.5%, by weight, of the coal, a ferruginous material need not be employed, but in some cases, improved results are obtained by the use of a desulfurizing amount of a ferruginous material. If the coal used in preparing the coke does not contain pyrites, then, as in the case of coke produced from a petroleum feedstock, a ferruginous material is also used in effecting the desulfurization.

The ferruginous material is either iron and/or an oxide of iron (ferrous oxide and/or ferric oxide) and such ferruginous material may be employed in an impure state. Thus, for example, the ferruginous material may be added as taconite fines, iron ore, iron, etc. In general, the ferruginous material, if employed, is in a finely divided state, e.g., a particle size of -100 mesh with 50% or more being -325 mesh and is present in an amount to provide a ferruginous material to coke weight ratio of from 5:95 to 25:75, and preferably from 10:90 to 15:85.

In accordance with a particularly preferred embodiment of the present invention, in addition to the ferruginous material, if employed, the coke is admixed with a desulfurizing amount of promoting additive which is either sulfuric acid, ferric sulfate or mixtures thereof in that the presence of such an additive has been found to promote desulfurization of the coke with the desulfurizing gas. The sulfuric acid and/or ferric sulfate additive is generally employed in an amount from about 1% to about 8%, and preferably in an amount from about 3% to about 8%, all by weight, based on coke. In some cases, i.e., cokes of higher sulfur content produced from petroleum feedstocks, in order to achieve the desired amount of desulfurization, it may be necessary to use sulfuric acid and/or ferric sulfate as a promoting additive in order to produce the desired degree of desulfurization.

The desulfurization is effected in a reducing atmosphere at a coke temperature from 1200°F. to 1800°F. and preferably at a temperature from 1400°F. to 1800°F., with a temperature of 1500°F. being generally preferred. (The furnace or oven in which the desulfurization is effected is generally at a temperature which is 100°F. higher than the temperature of the coke). The desulfurization with phosgene or a mixture of carbon monoxide and chlorine can not be effectively employed at coke temperatures in the order of 1900°F. and higher and, accordingly, in general, the temperature of the coke does not exceed 1800°F. The coke is maintained at the desulfurization temperature for a time sufficient to reduce the sulfur content of the coke to no greater than 0.85%, and preferably no greater than 0.5%. The precise time required for such desulfurization will vary with the amount of sulfur originally present in the coke and the distribution, as to type, of the sulfur; i.e., pyritic, sulfate, sulfide, or organic. In general, the time is at least one-half hour, with the time period generally not exceeding 16 hours.

Typically, the required desulfurization time is in the order of 1 to 8 hours.

The coke which is desulfurized in accordance with the present invention may be a coke produced from any one of a wide variety of carbonaceous coking feedstocks, including both liquid feedstocks derived from

either petroleum sources, such as reduced crudes, gilsonite, tar sand bitumens and the like or coal sources, such as coal tar pitch or coal tar and solid feedstocks, such as coal. The ferruginous material and/or promoting additive, if employed, may be admixed with the coking feedstock prior to coking or may be admixed with the coke product from a coking process. The coke, is then contacted with the desulfurizing gas (phosgene or a mixture of carbon monoxide and chlorine).

If a promoting additive and ferruginous material are employed, the ferruginous material is preferably pugged or sprayed with an aqueous solution of the promoting additive and the ferruginous material then mixed with the coking feedstock or coke. Alternatively, in the case where the coking feedstock is a solid or the ferruginous material is added to a previously produced coke, a mixture of the carbonaceous material and ferruginous material may be sprayed or pugged with an aqueous solution of the promoting additive.

The manner in which the coke is produced forms no part of the present invention and any one of a wide variety of coking procedures may be employed for producing the coke which is to be desulfurized. Thus, for example, a liquid carbonaceous feedstock, may be coked in a delayed or fluid coker, as known in the art, or in a carbonizer; e.g., an indirect-fired kiln type carbonizer, as known in the art. Coal may be carbonized in high temperature, slot-type coke ovens. Alternatively, the coal may be subjected to preheating and partial oxidation in a rabbled multiple-hearth furnace, followed by carbonization in one or more kiln-type carbonizers. As a further alternative, the coal may be agglomerated, for example by briquetting, preheated and partially oxidized in a grate-kiln or rabbled unit and carbonized in a kiln, a grate kiln or a circular grate type unit.

The desulfurization is generally effected in either a kiln or a fluid bed, a rabbled multiple hearth type furnace or a fixed bed with multiple gaseous reactant inlets. The choice of a suitable unit (the unit must be capable of maintaining vapor type integrity) is deemed to be within the scope of those skilled in the art.

The invention will be further described with respect to the accompanying drawing which schematically indicates various procedures for practising the present invention.

Solid or liquid carbonaceous coking feed may be premixed with, if employed, ground ferruginous material or a ferruginous material which has been previously mixed with an aqueous solution of ferric sulfate and/or sulfuric acid and dried. The carbonaceous feed is then coked or carbonized, and if the ferruginous material has been added to the coking feedstock, or is not required, e.g., some coals, the coke is desulfurized with phosgene or a mixture of carbon monoxide and chlorine in a desulfurization unit.

If the coke produced in the coke production unit does not include ferruginous material and a ferruginous material is to be added, the coke is ground and blended with ground ferruginous material or ferruginous material which has been previously blended with an aqueous solution of ferric sulfate and/or sulfuric acid and dried. The coke including the ferruginous material is then desulfurized by contact with phosgene or a mixture of carbon monoxide and chlorine.

The desulfurized coke is then washed and dried for use as a low sulfur coke or the washed and dried coke is ground and subjected to magnetic separation to produce a low-sulfur, low ash coke.

The invention will be further described with respect to the following examples, but it is to be understood that the scope of the invention is not to be limited thereby.

#### EXAMPLE I

Green coke, produced from a petroleum source, having a sulfur content in the order of 4.7% to 4.9% is desulfurized using a mixture of carbon monoxide and chlorine. Runs 1, 6, 7 and 9 are not effected in accordance with the present invention (Run 6 is effected without ferruginous material or additive; Runs 1 and 7 are effected at too high of a temperature; and Run 9 is effected with a promoting additive, but without ferruginous material).

TABLE I

Run	Coke Mix — Wt. %			Gas Composition -MOL. Percent	Run Conditions T, °F. (Coke)	Time at T, Hrs.	Sulfur in Product Coke %
	Green Coke	Taconite	Additive				
1	78	14	8-(H <sub>2</sub> SO <sub>4</sub> )	CO-25 Cl <sub>2</sub> -25 N <sub>2</sub> -49.5 O <sub>2</sub> -0.5	1900	6.0	1.06
2	78	14	8-(H <sub>2</sub> SO <sub>4</sub> )	CO - 12.5 Cl <sub>2</sub> - 12.5 N <sub>2</sub> - 74 O <sub>2</sub> - 1	1500	6.0	0.21
3	82	14.4	3.6-Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	CO - 12.5 Cl <sub>2</sub> - 12.5 N <sub>2</sub> - 74 O <sub>2</sub> - 1	1500	6.0	0.42
4	82	14.4	3.6-H <sub>2</sub> SO <sub>4</sub>	CO - 50 Cl <sub>2</sub> - 50	1500	4.0	0.47
5	82	14.4	3.6-Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	CO - 33 Cl <sub>2</sub> - 33 N <sub>2</sub> - 32.5 O <sub>2</sub> - 1.0	1500	4.0	0.47
6	100	—	—	CO - 15 Cl <sub>2</sub> - 15 N <sub>2</sub> - 69 O <sub>2</sub> - 1	1500	4.0	3.15
7	81	14.3	4.7-H <sub>2</sub> SO <sub>4</sub>	CO - 25	1900	3.5	1.74

TABLE I—Continued

Run	Coke Mix — Wt. %		Additive	Gas Composition -MOL Percent	Run Conditions T, °F. (Coke)	Run Conditions Time at T. Hrs.	Sulfur in Product Coke %
	Green Coke	Taconite					
8	82	14.4	3.6-H <sub>2</sub> SO <sub>4</sub>	Cl <sub>2</sub> - 12.5 SO <sub>2</sub> - 12.5 N <sub>2</sub> - 49 O <sub>2</sub> - 1 CO - 15 Cl <sub>2</sub> - 15 N <sub>2</sub> - 70	1500	4	0.52
9	92	—	8-H <sub>2</sub> SO <sub>4</sub>	CO - 15 Cl <sub>2</sub> - 15 N <sub>2</sub> - 70	1500	4	2.4

## EXAMPLE II

Coal (100 percent — 10 mesh) is contacted with the gaseous reactant in a fixed bed in a tubular reactor as reported in Table II. The coal is Illinois No. 6 having 4.17% sulfur and the space velocities are in the order of 1 to 3. Run 4 is not effected in accordance with the invention.

For possible use in carbon and graphite manufacture, wherein the ash content of the coke should be less than one percent, the coke after desulfurization is washed and magnetically separated to meet the necessary sulfur and ash requirements.

Numerous modifications and variations of the present invention are possible in light of the above teach-

TABLE II

Run	Coal Mix — Wt. %		Gas Composition - Mol Percent	Run Conditions T, °F. (Coke)	Run Conditions Time at T. Hrs.	Sulfur in Product, %
	Coal	Additive				
1	100	—	CO - 12.5 Cl <sub>2</sub> - 12.5 N <sub>2</sub> - 74 O <sub>2</sub> - 1	1500	4	0.4
2	100	—	CO - 12.5 Cl <sub>2</sub> - 12.5 N <sub>2</sub> - 75	1500	4	0.5
3	90	10-H <sub>2</sub> SO <sub>4</sub>	CO - 12.5 Cl <sub>2</sub> - 12.5 N <sub>2</sub> - 74 O <sub>2</sub> - 1	1500	4	0.26
4	100	—	—	1500	4	1.25

The present invention is particularly advantageous in that a coke having a sulfur content of no greater than 0.85%, and preferably no greater than 0.5%, may be produced from a wide variety of feedstocks having a wide variety of sulfur contents including those having sulfur contents of 4 percent or greater.

The process of the present invention, depending on the initial sulfur content of the feedstock employed in producing the coke, is capable of providing greater than 90% desulfurization of feedstocks having sulfur contents of 4% and greater.

For fuel applications, the desulfurized coke from the above treatment may be burned directly as a pulverized fuel with the potential of satisfying anti-pollution requirements with no further precautions. Depending on the non-ferruginous additive employed, some benefit may derive from first washing the coke to remove any residual water soluble additives from the coke. If a low-ash fuel is required, magnetic separation will effect the elimination of residual ferruginous materials.

When applied as a reductant where ferruginous values are indigenous to the process, this desulfurized coke, after particle size and temperature adjustment can be added directly to the pelletizers to adjust the integral carbon in the pellets to the level required for high or moderately high prereduction, permitting attainment of the desired sulfur levels in the finished pellets.

ings and, therefore, within the scope of the appended claims, the invention may be described otherwise than as particularly described.

What is claimed:

1. A process for desulfurizing coke, comprising:

contacting the coke with a desulfurizing gas comprising a member selected from the group consisting of phosgene and a mixture of carbon monoxide and chlorine, said contacting being effected at a coke temperature from 1200°F. to 1800°F. for a time sufficient to produce a coke with a sulfur content of no greater than 0.85%, said coke being admixed with a ferruginous material comprising a member selected from the group consisting of oxides of iron, iron and mixtures thereof for desulfurizing a coke prepared from petroleum and non-pyrites containing coal feedstocks.

2. The process of claim 1 wherein the coke which is desulfurized is produced from a petroleum feedstock and the coke is admixed with a desulfurizing amount of a ferruginous material during said contacting with the desulfurizing gas.

3. The process of claim 2 wherein the coke is further admixed with a desulfurizing amount of a desulfurizing promoter comprising a member selected from the group consisting of sulfuric acid, ferric sulfate and mixtures thereof.

4. The process of claim 3 wherein the coke temperature is from 1400°F. to 1800°F.

5. The process of claim 4 wherein the ferruginous material is present in a ferruginous material to coke weight ratio from 5:95 to 25:75.

6. The process of claim 5 wherein the desulfurizing gas is a mixture of carbon monoxide and chlorine.

7. The process of claim 6 wherein the desulfurizing promoter is present in an amount from about 1% to about 8%, by weight, of the coke.

8. The process of claim 1 wherein the coke which is desulfurized is produced from a pyrites containing coal feedstock.

9. The process of claim 8 wherein the coke is admixed with a desulfurizing additive comprising a member selected from the group consisting of sulfuric acid, ferric sulfate and mixtures thereof.

10. The process of claim 9 wherein the coke contacting temperature is from 1400°F. to 1800°F.

11. The process of claim 10 wherein the desulfurizing gas is a mixture of carbon monoxide and chlorine.

12. The process of claim 10 wherein the desulfurizing additive is present in an amount from about 1% to about 8%, by weight, of the coke.

13. The process of claim 12 wherein the coke is further admixed with a desulfurizing amount of a ferruginous material selected from the group consisting of oxides of iron, iron and mixtures thereof.

14. The process of claim 7 wherein the coke is maintained at a temperature from 1400°F to 1800°F to produce a coke having a sulfur content of no greater than 0.85%.

15. The process of claim 14 wherein the ferruginous material admixed with coke has a particle size of -100 mesh with at least 50% being -325 mesh.

16. The process of claim 11 wherein the coke is maintained at a temperature from 1400°F to 1800°F to produce a coke having a sulfur content of no greater than 0.85%.

17. The process of claim 13 wherein the ferruginous material has a particle size of -100 with at least 50% being -325 mesh.

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