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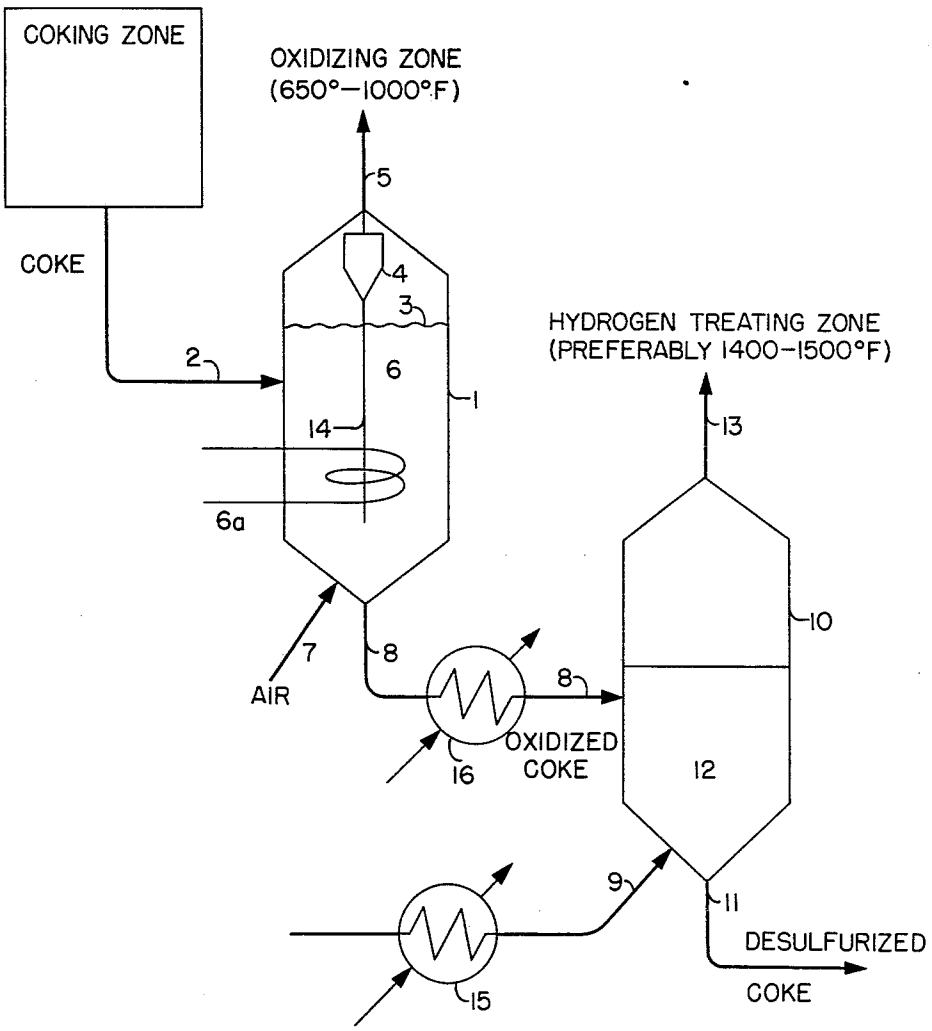

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DESULFURIZATION OF FLUID COKE WITH OXYGEN AND HYDROGEN

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This invention relates to improvements in desulfurizing and activating coke particles containing high percentages of sulfur. More particularly, it relates to the desulfurization of high sulfur petroleum coke particles from the fluid coking process by subjecting the coke particles to low temperature oxidation with an oxygen-containing gas followed by a hydrogen treatment both at controlled temperatures. It also relates to an improved low temperature oxidation conditioning treatment of these fluidized coke particles.

There has recently been developed an improved process known as the fluid coking process for the production of coke and the thermal conversion of heavy hydrocarbon oils to lighter fractions. The fluid coking unit consists basically of a reaction vessel or coker and a heater or burner vessel. In a typical operation the heavy oil to be processed is injected into the reaction vessel containing a dense turbulent fluidized bed of hot inert solid particles, preferably coke particles. Uniform temperature exists in the coking bed. Uniform mixing in the bed results in virtually isothermal conditions and effects instantaneous distribution of the feed stock. In the reaction zone the feed stock is partially vaporized and partially cracked. Product vapors are removed from the coking vessel and sent to a fractionator for the recovery of gas and light distillates therefrom. Any heavy bottoms is usually returned to the coking vessel. The coke produced in the process remains in the bed coated on the solid particles. Stripping steam is injected into the stripper to remove oil from the coke particles prior to the passage of the coke to the burner.

The heat for carrying out the endothermic coking reaction is generated in the burner vessel. A stream of coke is transferred from the reactor to the burner vessel employing a standpipe and riser system; air being supplied to the riser for conveying the solids to the burner. Sufficient coke or carbonaceous matter is burned in the burning vessel to bring the solids therein up to a temperature sufficient to maintain the system in heat balance. The burner solids are maintained at a higher temperature than the solids in the reactor. About 5% of coke, based on the feed, is burned for this purpose. This may amount to approximately 15% to 30% of the coke made in the process. The unburned portion of the coke represents the net coke formed in the process and is withdrawn.

Heavy hydrocarbon oil feeds suitable for the coking process are heavy or reduced crudes, vacuum bottoms, pitch, asphalt, other heavy hydrocarbon petroleum residua or mixtures thereof. Typically, such feeds can have an initial boiling point of about 700° F. or higher, an A. P. I. gravity of about 0° to 20°, and a Conradson carbon residue content of about 5 to 40 wt. percent. (As to Conradson carbon residue see ASTM Test D180–52.)

It is preferred to operate with solids having an average particle size ranging between 100 and 1000 microns in diameter with a preferred average particle size range between 150 and 400 microns. Preferably not more than 5% has a particle size below about 75 microns, since small particles tend to agglomerate or are swept out of the system with the gases.

The method of fluid solids circulation described above is well known in the prior art. Solids handling technique is described broadly in Packie Patent 2,589,124, issued March 11, 1952.

Fluid coking has its greatest utility in upgrading the quality of low grade vacuum residua and pitches from highly asphaltic and sour crudes. Such residua frequently contain high concentrations of sulfur of 3% or more and the coke product produced from these high sulfur feeds are also high in sulfur content. In general the sulfur content of the coke product from the fluid coking process may be in the range of 1 to 2 times the sulfur content of the residum feed from which it is produced. The sulfur content of coke from sour residua may range from 5 to 8% sulfur or more. The high sulfur content of the coke product poses a major problem in its efficient utilization. For most non-fuel or premium fuel uses a low sulfur content coke, below about 3 wt. percent sulfur, or at most about 4 wt. percent sulfur, is required. For example, low sulfur content coke is desired for the manufacture of phosphorous, for the production of calcium carbide, for lime burning in the manufacture of soda ash or other alkalis, for various metallurgical application, for the production of electrode carbon for various electrochemical applications such as the manufacture of aluminum and the like. Heretofore the sulfur content of high sulfur cokes from various sources has been reduced by a high temperature calcination in the range of about 2100° F. to 2800° F. in the presence of various gases such as flue gases, nitrogen, hydrogen, steam, and the like. However, this method of reducing sulfur is undesirably expensive due to the high temperatures required and the necessity of employing expensive refractory materials in the construction of the calciners. The sulfur content of cokes has also been reduced by treatment with hydrogen gas at somewhat lower temperatures in the range of 1200° to 1800° F. However, this method of treatment is also undesirably expensive due to the slow rate at which the sulfur is removed and the long treating time required to obtain the desired low level of sulfur content when starting with a high sulfur content raw coke.

The problem is even further complicated in the treatment of fluid petroleum coke because of the mentioned possibly higher than normal sulfur content from high sulfur feeds. In addition, the fact that the coke particles are built up by the continuous superposition of layers makes for much greater difficulty in sulfur removal without decreasing the coke yields.

The invention provides an improved process for desulfurizing coke, particularly high sulfur containing fluid petroleum coke particles wth gaseous reagents. The process comprises subjecting the coke particles in the form of a dense turbulent fluidized bed to a low temperature oxidation treatment with an oxygen-containing gas followed by a controlled hydrogen treatment. The sulfur content is consequently reduced to below 3 weight per cent by this treatment. As will be shown below, treating conditions outside those stipulated result in inferior results as do treatments with either hydrogen or oxygen alone.

The treatment with the oxygen-containing gas is conducted at a temperature of 600°–1000° F., preferably 650°–850° F. This low temperature oxidation treatment is preferably carried out while the coke particles are in the form of a dense turbulent fluidized bed. While it may be possible to effect the desired result of the low temperature oxidation by treatment of a fixed bed or moving fixed bed of coke with an oxygen-containing gas, the problem of removing the heat of reaction from a fixed bed, except in the case of very small fixed beds, makes the control of temperature very difficult in this type of operation. In contrast to a fixed bed, the temperature of oxidation is very easily controlled when oxidizing coke in a fluid bed by treatment with an oxygen-containing gas. The temperature may be controlled by means of coils immersed in the fluid bed. It is in-

deed surprising that these low temperature levels are necessary and that higher temperatures produce worse results as the reverse would normally be expected. The oxygen-containing gas can be atmospheric air or air enriched with oxygen at atmospheric or superatmospheric pressures. The time of the oxygen treatment can range broadly within the range of 15 minutes to 50 hours as will depend on the temperature and the oxygen concentration and pressures. When conducting the pre-oxidation at the higher temperatures of about 800°–1000° F. within the operable range, it may be preferred to employ air deficient in oxygen such as air diluted with steam, nitrogen, flue gas, or the like. If desired a part of the exit gases from the oxidation may be recycled to the oxidation zone. The best control feature within these ranges is the yield loss of the coke subjected to the oxidation. The conditions are controlled within the preceding ranges so that a maximum yield loss of 20 weight per cent, preferably 10 weight per cent, or conversely a minimum yield of 80, preferably 90 weight per cent, is obtained. For certain special applications of the low temperature oxidized coke or desulfurized coke it may be desirable to oxidize to a greater extent, for example, to a yield of 50% to 60%; however, for most cases yields below about 80% are uneconomical. The low temperature oxidation is a non-catalytic reaction and it is not necessary to add a catalyst to the system. In the low temperature oxidation a part of the coke, 2% to 20% or more, preferably 3% to 10%, is converted to its ultimate combustion products of carbon dioxide and water. Small amounts of carbon monoxide and sulfur dioxide are also produced as combustion products in the low temperature oxidation. Those skilled in the art will be able to easily obtain the desired sulfur reduction by combining the oxidation treatment with the hydrogen treatment described hereafter.

The hydrogen treatment is conducted at a temperature of about 1200°–1700° F., preferably at 1400°–1500° F. at atmospheric pressures or above. The coke is contacted at suitable temperature and pressure with a flow of hydrogen which sweeps the hydrogen sulfide product out of the hydrogen treatment zone. The minimum flow of hydrogen utilized is about 100 v./v./hr. (volumes of hydrogen per volume of coke per hour). If desired the hydrogen leaving the hydrogen treatment zone may be scrubbed or otherwise treated by known means to remove or recover hydrogen sulfide and recycled to the hydrogen treatment zone. The treatment of the preoxidized coke with hydrogen is a non-catalytic process and it is not necessary to add a catalyst to the system. The time of treating is in the range of 10 minutes to about 10 hours, although the time is not critical. In contrast with the preceding oxygen treatment, the hydrogen treatment may be advantageously conducted while the coke particles are in a fixed bed or a moving fixed bed. Since the heat of reaction in the hydrogen treatment is relatively small and the control of temperature is less critical than in the oxygen treatment, a fixed bed may be employed. However, a fluid bed type operation may also be employed for the hydrogen treatment. The choice of the method of contacting the coke with hydrogen will often depend upon the type of equipment available for this operation.

The hydrogen-containing gas can be obtained from the gas produced in the coker after removal of most of the hydrocarbons formed in the coking operation. Other sources of hydrogen include the pure gas or the tail gas from a hydroformer. The hydrogen-containing gas is preferably treated in the conventional manner to remove hydrogen sulfide and other sulfur-containing compounds before use.

This invention will be better understood by reference to the flow diagram shown in the drawing.

In the drawing, numeral 1 represents a reactor constructed of suitable materials for operation at temperatures of 600°–1000° F. A bed of coke particles 6 is contained therein and reaches an upper level indicated by number 3. The bed is maintained in the form of a dense turbulent fluidized bed by air entering the vessel via line 7. The fluidizing gas passes upwardly at a velocity of 0.5–2.0 ft./sec., establishing the solids at the indicated level.

Coke particles for the desulfurization treatment enter the reactor through line 2. They can be fed directly from the fluid coke reaction system or from a final product coke inventory. The temperature of fluid bed 6 is maintained at the desired level within the range of 600°–1000° F., preferably 650°–850° F., by means of cooling coil 6a immersed in fluid bed 6. The flue gas comprising nitrogen, water, carbon dioxide, small amounts of carbon monoxide and sulfur dioxide, and unconsumed oxygen passes upwardly through the bed and is removed from the vessel via line 5 after passing through cyclone 4 from which solids are returned to the bed via dipleg 14.

A stream of oxidized coke particles is removed from the oxidizing zone via line 8 into hydrogen-treating zone 10. The temperature is maintained within a preferred range of 1400°–1500° F. The drawing shows the oxidized coke particles in the form of a falling or descending fixed bed 12 in hydrogen-treating zone 10; however, if preferred, hydrogen treatment zone 10 may comprise one or more fluid beds of the oxidized coke particles. Hydrogen-containing gas enters the vessel 10 through line 9. The gases leaving through line 13 contain hydrogen sulfide and may contain some methane and other hydrocarbon gases in addition to unconsumed hydrogen. The low temperature oxidized coke entering hydrogen treating zone 10 by line 8 may be preheated to a temperature about 50° to 200° F. below the desired hydrogen treating temperature by passage through heating zone 16. Upon entering zone 10 the coke is further heated to the desired hydrogen treating temperature by a momentary strongly exothermic reaction which occurs when the low temperature oxidized coke is first contacted by hydrogen. While this exothermic reaction of short duration is not fully understood, it may be the combination of hydrogen with oxygen adsorbed on the coke surface. Heating zone 14 may comprise a coil in a furnace or other heating means. Heat may also be supplied to hydrogen treating zone 10 by preheating the hydrogen in line 9 by passage through heating zone 15. Heating zone 15 may comprise a coil in a furnace, or a heat exchanger for recovery of heat from desulfurized coke in line 11, or other heating means. When coke bed 12 comprises a fluid bed, heat may also be supplied to hydrogen treating zone 10 by means of a heating coil immersed in bed 12. Hot combustion gases may be passed through the heating coil to supply heat. Desulfurized coke product is removed through line 11.

The following examples further show the advantages of this invention.

EXAMPLE 1

To illustrate a prior art process for the removal of sulfur from coke and to obtain data for comparison to show the advantages of the process of the present invention, samples of raw coke were treated with hydrogen at several temperatures without prior preoxidation at low temperature. The raw coke employed comprised 7 weight per cent sulfur and was obtained by the fluid coking process when feeding a vacuum residuum from the vacuum distillation of crude petroleum from the Hawkins field. The hydrogen treatment was conducted at atmospheric pressure at a hydrogen flow rate of about 1500 v./v./hr. employing a fixed bed of the raw coke. Table I shows the sulfur content of the hydrogen treated coke after various time intervals of hydrogen treatment at the indicated temperatures. These data show that over the range of 1000° to 2400° F. the rate of sulfur removal from the raw coke is most rapid at about 1300° F. The data

further show that even under this most favorable condition the rate of sulfur removal by the prior art process is extremely slow and the coke still contains 3.5 weight per cent sulfur after five hours treatment with a flow of hydrogen at 1300° F. Extrapolation of these data indicates that it is impossible to obtain a product of less than about 3 weight per cent sulfur by this method of treatment regardless of the length of time employed.

Table I.—Treatment of raw coke (7% S) with hydrogen

[Atmospheric pressure, 1,500 v./v./hr.]

Column	1	2	3	4	5	6	7	8
Temperature, ° F	1,000	1,200	1,300	1,400	1,600	1,800	2,100	2,400
Percent S remaining after 0.5 Hr	6.8	5.9	5.6	5.8	5.9	6.7	6.5	4.9
Percent S remaining after 1 Hr	6.7	5.5	5.1	5.4	5.6	------	------	------
Percent S remaining after 2 Hrs	------	4.9	4.4	4.9	5.3	------	------	------
Percent S remaining after 5 Hrs	------	4.1	3.5	4.6	5.2	6.7	6.4	------

EXAMPLE 2

To illustrate the effect of low temperature oxidation without hydrogen treatment on the properties of coke, samples of coke containing 7 weight per cent sulfur from fluid coking of Hawkins residuum were oxidized at various temperatures to various yield levels. The oxidation was accomplished by treatment of a fluid bed of coke with air at atmospheric pressure at the desired temperature for the period of time required to give the desired yield of oxidized coke. The data obtained are shown in Table II. For comparison data are also shown for the raw unoxidized coke and for a sample of coke oxidized at 1100° F. Comparison of the data in columns 2, 3, 4, 5, 6, and 7 with column 1 clearly shows that oxidation within the preferred temperature range of 650° to 850° F. results in a slight reduction of the sulfur content, a large increase in the surface area, and a substantial increase in the real density of the coke. On the other hand, a comparison of the data in column 8 with column 1 shows that oxidation at 1100° F., which is outside the range of the present invention, actually causes an increase in the sulfur content of the coke due to the preferential burning of carbon relative to sulfur at this higher temperature, and an actual loss of surface area, and little or no improvement in the true density of the coke. Comparison of the data in columns 2, 3, 5, and 7 show that, in general, the lower the oxidation temperature within the preferred range, the greater the improvement in coke properties. Comparison of columns 3 and 4 and of columns 5 and 6 show that, in general, the lower the yield upon oxidation, the greater the improvement in coke properties. However, in general, it is preferred to oxidize to yields greater than about 80%.

EXAMPLE 3

To illustrate the improvement in desulfurization attained by the combined low-temperature-oxidation and hydrogen treatment, samples of coke containing 7 weight per cent sulfur from fluid coking of Hawkins residuum were pre-oxidized and then treated with hydrogen. The oxidation was accomplished by treatment of a fluid bed of coke with air at atmospheric pressure at the desired temperature for the period of time required to give the desired yield of pre-oxidized coke. The pre-oxidized coke was treated with hydrogen at atmospheric pressure at a temperature of 1300° F. at a hydrogen flow rate of about 1500 v./v./hr. employing a fixed bed of the pre-oxidized coke. Table III shows the sulfur content of the hydrogen treated coke after various time intervals of hydrogen treatment.

For comparison data are included in column 1 of the table for the hydrogen treatment of raw (un-pre-oxidized) coke and in column 8 for the hydrogen treatment of coke pre-oxidized at 1100° F., which is outside the critical temperature range for desulfurization. Comparison of the data of columns 2, 3, 4, 5, 6, and 7 with column 1 clearly shows the improved desulfurization when hydrogen treating coke pre-oxidized in the preferred temperature range of 650° to 850° F. The data of column 8 show that hydrogen treatment of coke pre-oxidized at 1100° F. is only slightly better, if any, for sulfur removal than hydrogen treatment of raw coke. Pre-oxidation at 1100° F. is outside the critical temperature range for sulfur removal. Comparison of columns 2, 3, 5, and 7 show that at constant, or nearly constant, levels of yield the lower the temperature of pre-oxidation within the preferred temperature range the better the desulfurization upon subsequent treatment with hydrogen. Comparison of columns 3 and 4 and of columns 5 and 6 show that the degree of improvement attainable at the lower temperatures within the preferred range may also be attained at the higher temperatures within the preferred range by taking lower pre-oxidized coke yields, again within the specified range.

Table II—Properties of low temperature oxidized (7% S)

Column	1	2	3	4	5	6	7	8
Oxidation Conditions:								
Temperature, ° F	None	650	700	700	750	750	850	1,100
Time, Hrs	0	16	5	23	2	4.2	1.5	1
Yield, wt. percent	100	93	93	55	94	80	91	93
Properties of Oxidized Coke:								
Wt. Percent Sulfur	7	6.7	6.7	5.6	6.3	6.2	6.4	7.2
Surface Area, M^2/g	5	136	133	358	98	199	83	2
True Density	1.55	1.63	1.63	1.88	1.73	------	1.61	1.60

Table III.—Desulfurization of coke (7% S)

PRE-OXIDATION

Column	1	2	3	4	5	6	7	8
Temperature, ° F	None	650	700	700	750	750	850	1,100
Yield, Wt. Percent	100	93	93	62	94	80	91	93

HYDROGEN TREATMENT AT 1,300° F. AND 1500 v./v./hr.

Percent S remaining after 0.5 Hr	5.6	3.3	3.3	2.8	4.4	3.6	4.2	5.3
Percent S remaining after 1 Hr	5.1	2.6	2.9	2.4	3.8	2.8	3.6	4.6
Percent S remaining after 2 Hrs	4.4	2.0	2.3	2.2	3.2	2.3	3.0	4.0
Percent S remaining after 4 Hrs	3.7	1.7	2.2	2.0	2.5	2.1	2.8	3.6

EXAMPLE 4

Samples of coke containing 7 weight per cent sulfur from fluid coking of Hawkins residuum were pre-oxidized and then treated with hydrogen. The oxidation was accomplished by treatment of a fluid bed of coke with air at the desired temperature for the period of time required to give the desired yield of pre-oxidized coke. The pre-oxidized coke was treated with hydrogen at various temperatures at a hydrogen flow rate of about 1500 v./v./hr. employing a fixed bed of the pre-oxidized coke. Table IV shows the sulfur content of the hydrogen treated coke after various time intervals of hydrogen treatment. The data show that the sulfur removal from the pre-oxidized coke is most favorable when the hydrogen treatment is conducted in the preferred temperature range of about 1400° to 1500° F. This is in contrast to raw coke which, as shown in Table I, is desulfurized more readily by hydrogen treatment at about 1300° F., even though under this most favorable condition the raw or un-pre-oxidized coke is desulfurized with extreme slowness.

Table IV.—Desulfurization of coke (7% S)

PRE-OXIDATION

Column	1	2	3	4	5
Temperature, ° F	650	650	750	750	750
Yield, Wt. Percent	93	93	80	80	80

HYDROGEN TREATMENT AT 1,500 V./V./HR.

Temperature, ° F	1,300	1,400	1,300	1,400	1,500
Percent S remaining after 0.5 Hr	3.3	2.1	3.6	2.8	2.6
Percent S remaining after 1 Hr	2.6	1.4	2.8	2.2	2.1
Percent S remaining after 2 Hrs	2.0	1.1	2.3	1.9	1.9
Percent S remaining after 4 Hrs	1.7	0.9	2.1	1.7	1.8

EXAMPLE 5

Samples of coke containing 7 weight per cent sulfur from fluid coking of Hawkins residuum were pre-oxidized and then treated with hydrogen. The oxidation was accomplished by treatment of a fluid bed of coke with air at the desired temperature for a period of time required to give the desired yield of pre-oxidized coke. The pre-oxidized coke was treated with hydrogen at various temperatures and at 1 atmosphere and at 3.4 atmospheres pressure absolute employing a fixed bed of preoxidized coke. The hydrogen flow rate was adjusted to give approximately the same rate of displacement of gases in the reactor at the two levels of pressure. Table V shows the sulfur content of the hydrogen treated coke after one-half and one hour of hydrogen treatment. Comparison of columns 1 and 2 show that an increase in the partial pressure of the treating hydrogen gives a slight increase in the rate of sulfur removal.

Table V.—Desulfurization of Coke (7% S)

PRE-OXIDATION

Column	1	2	3	4
Temperature, ° F	650	650	700	700
Yield, Wt., Percent	93	93	62	62

HYDROGEN TREATMENT

Temperature, ° F	1,400	1,400	1,300	1,400
Pressure, Atmospheres Absolute	1	3.4	1	3.4
Hydrogen Rate, v./v./hr.[1]	1,500	4,550	1,500	4,550
Percent S remaining after 0.5 Hr	2.1	1.9	2.8	1.0
Percent S remaining after 1 Hr	1.4	1.3	2.4	

[1] Calculated to atmospheric pressure.

In summary, all the foregoing data show that the sulfur content can be reduced below 3 weight per cent and that, i. e., from 1 to 2½ weight per cent by the process of this invention.

In order to express this information more fully the following conditions of operation of the various fluid coking components are set forth below.

CONDITIONS IN FLUID COKER

	Broad Range	Preferred Range
Temperature, ° F	850–1,200	900–1,000
Pressure, Atmospheres	1–10	1.5–2
Superficial Velocity of Fluidizing Gas, Ft./Sec	0.2–2.0	0.5–1.0
Average Size of Coke Particles, Microns	100–1,000	150–400

CONDITIONS IN BURNER

	Broad Range	Preferred Range
Temperature, ° F	1,050–1,600	1,100–1,200
Superficial Velocity of Fluidizing Gas, Ft./Sec	1–5	2–4

As stated before, the process of this invention is particularly suitable and preferred for the desulfurization of fluidized coke derived from petroleum oils. It is applicable to other coke which is first reduced to the size for processing in the indicated manner.

The advantages of the process of this invention will be apparent to those skilled in the art. The sulfur content is reduced to acceptable levels by an easily controlled economical process and satisfactory yields are maintained.

The process is also applicable for the treatment of coke containing smaller quantities of sulfur. Several cycles of treating with an oxygen containing gas followed by hydrogen can be employed if desired.

It is to be understood that this invention is not limited to the specific examples which have been offered merely as illustrations and that modifications may be made without departing from the spirit of the invention.

What is claimed is:

1. A process for desulfurizing coke particles containing a high percentage of sulfur, which comprises the steps of treating the coke particles with an oxygen-containing gas at a temperature in the range of 600° to 1000° F. for from 15 minutes to 50 hours so as to obtain a minimum coke yield of 80 weight per cent and treating the thus oxidized coke with hydrogen at a temperature in the range of 1200° to 1700° F. with a minimum of 100 v./v./hr. of hydrogen whereby the sulfur content of the coke is reduced to below 3 weight per cent.

2. A process for desulfurizing coke particles containing a high percentage of sulfur, said particles having been produced by contacting a heavy petroleum oil coking charge stock at a coking temperature with a body of coke particles maintained in the form of a dense turbulent fluidized bed in a reaction zone, wherein the oil is converted to product vapors and carbonaceous solids are continuously deposited on the coke particles, removing product vapors from the coking zone; burning a portion of coke particles removed from the coking zone in a separate burning zone to increase the temperature of said fluidized particles, returning a portion of the heated coke particles from the burning zone to the coking zone and withdrawing product particles which comprises the steps of treating the coke particles with an oxygen-containing gas at a temperature in the range of 600°–1000° F. for from 15 minutes to 50 hours so as to obtain a minimum coke yield of 80 wt. percent and treating the thus oxidized coke with hydrogen at a temperature in the range of 1200°–1700° F. with a minimum of 100 v./v./hr. of hydrogen whereby the sulfur content of the coke is reduced to below 3 weight per cent.

3. The process of claim 2 in which the coke particles being treated with an oxygen-containing gas are in the form of a dense turbulent fluidized bed.

4. The process of claim 3 in which the oxygen-containing gas treating step is conducted at a temperature in the range of 650° to 850° F. so as to obtain a minimum coke yield of 90 weight per cent.

5. The process of claim 4 in which the hydrogen-treating step is conducted at a temperature in the range of 1400° to 1500° F. for from 10 minutes to 10 hours.

6. A process for conditioning and improving the surface characteristics of coke particles containing a high percentage of sulfur, said particles having been produced by contacting a heavy petroleum oil coking charge stock at a coking temperature with a body of coke particles maintained in the form of a dense turbulent fluidized bed in a reaction zone, wherein the oil is converted to product vapors and carbonaceous solids are continuously deposited on the coke particles; removing product vapors from the coking zone; burning a portion of coke particles removed from the coking zone in a separate burning zone to increase the temperature of said fluidized particles, returning a portion of the heated coke particles from the burning zone to the coking zone and withdrawing product particles which comprises treating the product coke particles with an oxygen-containing gas at a temperature in the range of 600°–1000° F. for from 15 minutes to 50 hours.

7. The process of claim 6 in which the minimum coke yield obtained is 80 weight per cent.

8. The process of claim 7 in which the oxygen-containing gas treating step is conducted at a temperature in the range of 650° to 850° F. so as to obtain a minimum coke yield of 90 weight per cent.

9. The process of claim 6 in which the product coke particles being treated with an oxygen-containing gas are in the form of a dense, turbulent, fluidized bed.

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