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2 Sheets-Sheet 1

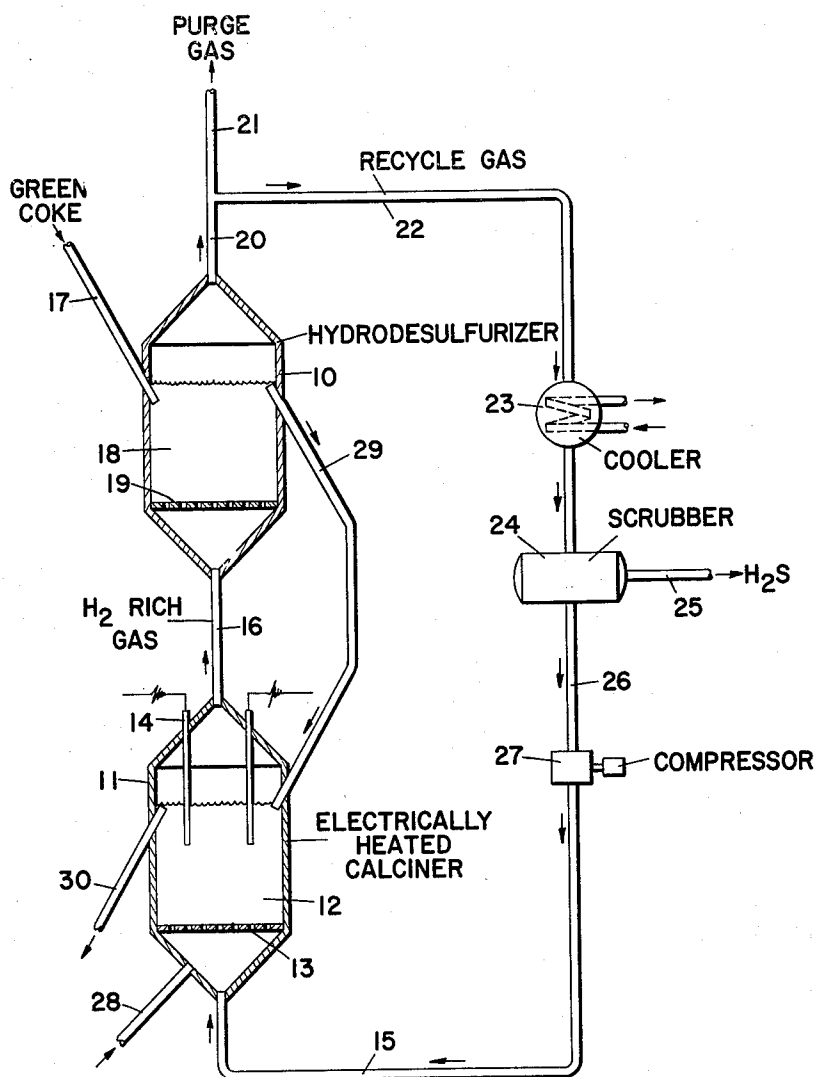


FIGURE 1

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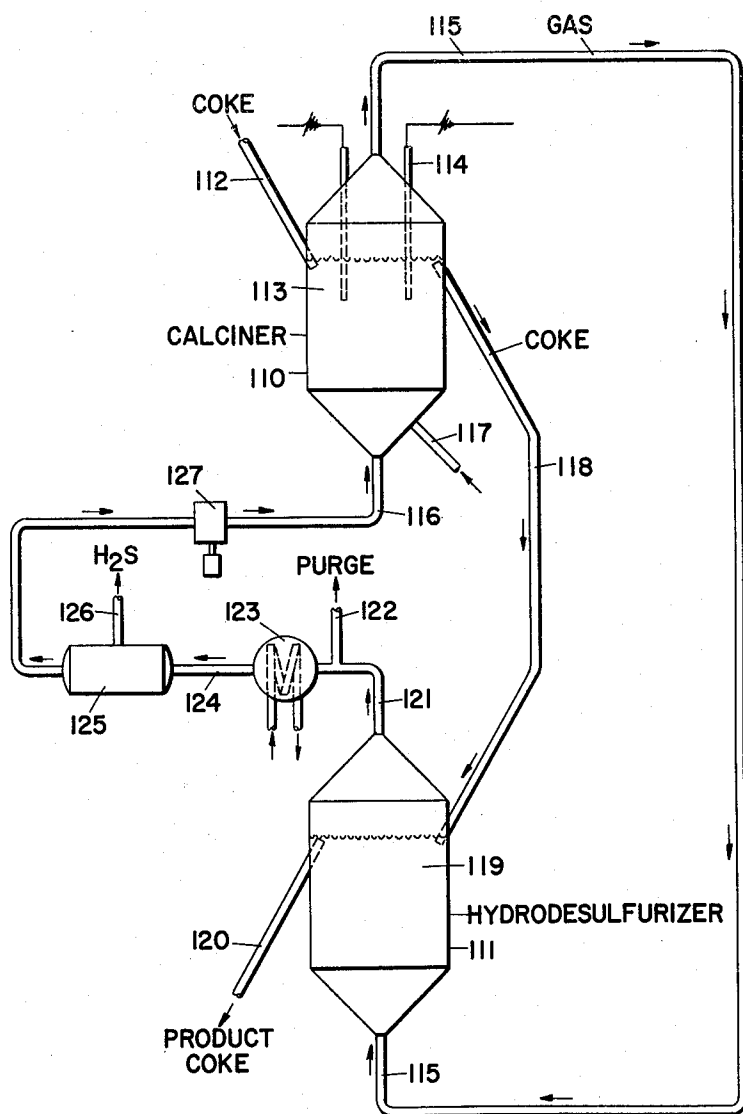


FIGURE-2

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TWO-STEP PROCESS FOR UPGRADING FLUID COKE

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This invention relates to improvements in calcining and
desulfurizing coke. More particularly, it relates to a
two-step process for calcining and desulfurizing coke by
means of an electrically heated solids bed.

There has recently been developed an improved process
known as the fluid coking process for the production of
fluid coke and the thermal conversion of heavy hydro-
carbon oils to lighter fractions, e.g., see Serial No.
375,088, filed August 10, 1953, now Patent No. 2,881,130,
granted April 7, 1959. For completeness the process is
described in further detail below, although it should be
understood that the fluid coking process itself is no part
of this invention.

The fluid coking unit consists basically of a reaction
vessel or coker and a heater or burner vessel. Transfer
line or fluid bed reactors and burners can be used.
Staged systems can be employed. 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 isothermal conditions and effects in-
stantaneous distribution of the feed stock. In the re-
action 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 re-
covery of gas and light distillation 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 in-
jected 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 re-
action is generated in the burner vessel, usually but not
necessarily separate. A stream of coke is thus trans-
ferred 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 added carbonaceous matter is burned in the burn-
ing vessel to bring the solids therein up to a tempera-
ture sufficient to maintain the system in heat balance.
The burner solids are maintained at a higher tempera-
ture 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 net coke production, which
represents the coke made less the coke burned, is with-
drawn.

Heavy hydrocarbon oil feeds suitable for the coking
process include heavy crudes, atmospheric and crude
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 A.S.T.M.
Test D-189-41.)

The fluid coke product particles have a particle di-
ameter predominantly, i.e., about 60 to 90 wt. percent, in
the range of 40 to 500 microns, a sulfur content about
3 wt. percent, in many cases above 5 wt. percent, and a
volatile content of 2 to 10 wt. percent. They have a
real density (average density of solid) of about 1.4 to

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1.7 gms./ccm. which is too low for use in the manufacture
of carbon electrodes for making aluminum and other
purposes. Increased density and lower sulfur and vol-
atile contents are particularly necessary before the fluid
coke is suitable for manufacture into these electrodes,
one of the major uses of petroleum coke. In addition,
calcined and desulfurized coke is a more saleable prod-
uct for use as foundry molds and other end uses.

It has heretofore been suggested that calcination and/
or desulfurization could be obtained by subjecting the
coke to elevated temperatures, a portion of the coke and/
or an extraneous fuel being burned to supply the requi-
site heat for the operation. Such high temperature
burning systems are relatively expensive.

It has very recently been suggested that fluid coke
could be heated to high temperatures by the use of an
electrically heated fluidized solids bed wherein heat is
generated by the electrical resistance of the coke par-
ticles. Such a system offers efficient utilization of
thermal energy as well as having a relatively low invest-
ment cost. Such an operation permits uniform heat
transfer with consequent uniform electrical heating, ease
of controlling solids transfer, and is particularly suited
to the treatment of relatively finely sized solids. It has
been appreciated that by maintaining fluid coke at tem-
peratures of 2200 to 3200° F., particularly 2600 to 2800°
F., the coke could thereby be simultaneously desulfurized
and calcined.

The present invention offers an improved method of
effecting desulfurization and calcination. It offers the
advantages of efficiency and low investment character-
istic of an electrically heated fluidized bed without neces-
sitating a very high temperature treating zone. In ac-
cordance with the present invention, both desulfurization
and calcination are effected under less severe reaction
conditions, consequently reducing the problem of mater-
ials construction, maintenance and heat input. A
major disadvantage of hydrodesulfurization in the prior
art systems was putting heat in at the high pressure used.
High pressure combustion requires very expensive air
compression. Electric heating has none of the above
disadvantages and is particularly suited to heating a high
pressure system. Whereas previous hydrodesulfurization
systems needed externally supplied hydrogen, which is
very expensive, the present process generates its own
H₂ at little added cost.

More specifically, in accordance with the present inven-
tion, fluid coke is treated in an electrically heated fluid
bed maintained at calcination temperatures of 1300 to
1900° F. The volatiles liberated by the electrical calcina-
tion will contain a substantial portion of hydrogen,
e.g. at least 50 vol. percent, since raw fluid coke generally
contains 1.0 to 3.0 wt. percent hydrogen. The hot gasi-
form released materials are then passed to a treating zone
containing high sulfur fluid coke. The gases maintain the
coke in the form of a fluidized bed at a temperature of
1300 to 1500° F. They serve to heat, fluidize, and de-
sulfurize the fluid coke. Under these conditions, i.e.
uniform temperature of at least about 1300° F., the
fluid coke is hydrodesulfurized to high yields of low sul-
fur coke. By circulating coke from one zone to the other,
the net fluid coke product will be both calcined, e.g. to
real densities of at least 1.8 gms./ccm., and desulfurized,
e.g. have less than 3 wt. percent sulfur.

Strict control over the conditions in the desulfurization
is required. A temperature of from about 1300 to
1500° F. is necessary in order to effect hydrodesulfuriza-
tion of the fluid coke. The present process eliminates the
need for extraneous hydrogen while simultaneously pro-
viding requisite hydrogen and sensible heat energy by
the electrically heated calcination of coke.

It is to be noted that desulfurization is accomplished

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by the liberated calciner gases under fluidized bed conditions. As opposed to a moving or fixed bed, the fluid bed gives uniform heat transfer throughout the solids and thus all solids simultaneously are maintained at requisite temperature for desulfurization, i.e. at least 1300° F. Merely heat exchanging calciner off-gases with an incoming, moving solids column or the like would not give bulk desulfurization since, at best, only a small cross section of the column might be heated to requisite desulfurization temperature, and even this section would not have a requisite contacting period. Further, no claim is herein made that the specific conditions of temperature and pressure employed in the desulfurization zone are novel, in themselves.

The various aspects and modifications of the present invention will be made more clearly apparent by reference to the following description, embodiments and accompanying drawings.

FIGURE 1 depicts a system wherein coke is first hydrodesulfurized prior to passing to the calcining zone;

FIGURE 2 illustrates a calcination treat preceding desulfurization.

Turning to FIGURE 1, the system shown basically comprises hydrodesulfurization zone 10 and calciner 11, containing fluidized solids beds 18 and 12, respectively. The feed to the system is "green" fluid coke, i.e. the untreated fluid coke product of the fluid coking system. In the embodiment described, it is the solid product resulting from the conversion of a South Louisiana crude and contains about 6.5 wt. percent sulfur while having a real density of about 1.5 gms./cc. The fluid coke ranges from about 50 to 500 microns in size.

In calciner 11, the fluid coke (after having been desulfurized as will later be described) is maintained at a temperature of about 1800° F. by means of electrodes 14 which impress a sufficient voltage, e.g. 100 to 500 volts to maintain the fluidized solids bed at calcining temperature due to the resistance heating of the coke particles. Electrodes 14 may be graphite or other conventional electrode materials connected to an A.C. or D.C. source. Fluidizing gas is supplied to the lower portion of the calcining zone by lines 28 and/or 15 and is distributed throughout the bed by grid 13 at an overall velocity of 0.1 to 3.0 ft./sec., the bed thus having a density of about 30-60 lbs./cu. ft. It is preferred to use recycle gas from which hydrogen sulfide has been removed as the fluidizing medium although an extraneous gas such as nitrogen may be introduced by line 28.

Continuously, or intermittently if desired, calcined fluid coke is withdrawn through line 30, its real density being substantially increased, e.g. to 1.8 gms./cc. or greater, over that of the green coke. It will also be low in sulfur content due to its previous treatment in zone 10 as will be described below.

The calcining zone serves to liberate volatile matter such as hydrogen and methane from the fluid coke, the hot liberated gases normally containing at least 50 volume percent hydrogen. The hot hydrogen-containing gases are withdrawn overhead and passed to hydrodesulfurizer 10 by means of line 16.

Zone 10 contains a bed of fluid coke particles. Generally, high sulfur coke fed to zone 10 by inlet 17 will be at a relatively high temperature, e.g. 1000° F., since it will be directly withdrawn from the fluid coking conversion system, preferably the burner thereof. The calciner off-gases heat bed 18 to a temperature of about 1300° F. while simultaneously fluidizing it. Additional fluidizing gas can be introduced if required, distributor 19 serving to uniformly distribute the gases. Hydrodesulfurizer 10 is preferably maintained at a pressure of about 50 to 200 p.s.i.g. The quantity of hydrogen present in the calciner volatiles is sufficient to give a hydrogen throughput of at least 150 volumes/volume of coke fed per hour to bed 18, preferably being in excess of 1500 v./v./hr. High hydrogen rates are readily maintained by

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recycling of the off-gases of hydrodesulfurizer 10 after removal of liberated sulfurous gases. In the embodiment illustrated, the solids have a residence time of 1 hour at a hydrogen throughput of 2000 v./v./hr.

At these conditions, the fluid coke particles fed to zone 10 undergo desulfurization in a highly expeditious manner, thereby reducing the sulfur content of the coke withdrawn by line 29 to less than 3 wt. percent, preferably of the order of 1 to 2 wt. percent. The coke may be recovered directly as a low sulfur product, but it is generally then passed to calciner 11 for carbonization of its volatile matter, the ultimate coke product therefore being an excellent material for use in electrodes, molding compositions, etc.

The gases liberated in hydrodesulfurizer 10 are withdrawn through outlet 20. It is generally preferred to use the non-sulfurous portion thereof for fluidizing zone 11. Therefore, a portion of the gases is purged through line 21 while the remainder is recycled to cooler 23 by line 22. After being cooled to a temperature of about 100° F., the gases are passed to scrubber 24 wherein they are contacted with diethanolamine or other conventional solvents, contact solids, etc., so as to remove hydrogen sulfide. The hydrogen sulfide is withdrawn from the circulation system through line 25 while the remaining gases are sent by line 26 to compressor 27 which serves to boost their pressure to about 90 p.s.i.g. The gases are then recycled to calciner 11. Sulfur, dust, etc. can also be removed by unit 24.

It is to be noted that the required conditions for effective, relatively low temperature hydrodesulfurization, per se, have recently been established in the art as requiring a temperature of about 1300 to 1500° F. For example, fluid coke having a sulfur content of 7.1 wt. percent was hydrodesulfurized at 75 p.s.i.g. with a hydrogen-containing gas for a period of 60 minutes, a hydrogen rate of 3500 v./v./hr. being employed. Although the same conditions (other than temperature) were employed in both runs, a hydrodesulfurization temperature of 1000° F. only served to reduce sulfur content to 6.3 wt. percent whereas a temperature of 1300° F. gave a fluid coke product of 2.1 wt. percent sulfur. Thus, temperatures of at least 1300° F. are required to give effective desulfurization.

Of course, the present invention offers numerous advantages over the prior art desulfurization methods since requisite hydrogen is liberated while simultaneously calcining the coke material in an extremely thermally efficient, electrically heated step, the two steps being therefore most advantageously integrated.

FIGURE 2 illustrates another modification of the present invention. In the system shown, green coke is fed directly to calciner 110 by line 112, and thus first undergoes calcination. Fluidized bed 113 is maintained in a highly turbulent state by means of recycle gas introduced by line 116 and/or extraneous fluidizing medium injected by line 117. Sufficient voltage is impressed across bed 113 by means of electrodes 114 to heat the bed to a temperature of 1800° F. due to the resistance heating of the solids.

Liberated volatile matter containing a substantial portion of hydrogen is taken overhead by line 115 and circulated to hydrodesulfurization zone 111 wherein it serves to heat, fluidize, and hydrodesulfurize fluid coke maintained as bed 119 in the manner described relative to FIGURE 1. The feed to unit 111 is, however, the calcined product of zone 110, the coke being circulated to the hydrodesulfurization zone by conduit 118. Unit 111 operates at a temperature of about 1400° F. and a pressure of 85 p.s.i.g. Approximately 2500 volumes of hydrogen (in the liberated volatiles stream) per volume of coke to be treated is employed under about a 30 minutes' residence time. Product coke having a sulfur content of about 1.0 wt. percent and a real density of 1.8 gms./cc. is recovered through line 120.

Sulfurous gases withdrawn by line 121 may be purged,

in part or totally, through line 122. It is generally desired to employ a portion of the gases as a recycle fluidizing medium and thus a portion of the gases are cooled in cooler 123 and passed to scrubber 125 by line 124, hydrogen sulfide being removed by any of numerous conventional solvents and recovered by outlet 126. The treated gases may then be compressed by unit 127 and circulated to zone 110 as fluidizing medium.

The following tabular presentation presents a compilation of data applicable to the systems described.

Table 1

Initial solids feed:		Preferred range
Size range, microns-----	50 to 500.	
Sulfur content, wt. percent----	3 or greater.	
Real density, gms./cc.-----	1.7 or less.	
Calcination zone:		
Temperature, ° F.-----	1300 to 1900.	
Voltage across electrodes, volts-----	100 to 500.	
Bed density, lbs./cu. ft.-----	30 to 60.	
Fluidizing gas velocity, ft./sec.-----	0.1 to 3.0.	
Vol. percent hydrogen in liberated volatiles-----	At least 50.	
Hydrodesulfurization zone:		
Temperature, ° F.-----	1300 to 1500.	
Pressure, p.s.i.g.-----	50 to 250.	
Hydrogen throughput, volume/volume of solids/hour	1500 or greater.	
Bed density, lbs./cu. ft.-----	30 to 50.	
Fluidizing gas velocity, ft./sec.-----	0.1 to 3.0.	
Treatment time-----	30 minutes or greater.	
Ultimate solids product:		
Wt. percent sulfur-----	About 2 or less.	
Real density, gms./cc.-----	At least 1.8.	

Numerous modifications may be made to the present invention. For example, the volatiles liberated in the calciner may contain considerably more hydrogen than is required in the desulfurization zone, and hence such excess hydrogen may be removed prior to passing the gasses to the desulfurization zone. If desired, temperature in the hydrodesulfurization zone may be further controlled by heat exchange coils or the like. The invention is particularly suited to the processing of fluid coke but it may also be applied to other cokes, coal, or carbonaceous material having similar desulfurization and calcination properties.

In summary, the present integrated process permits both calcination and desulfurization under relatively low temperature conditions. Requisite desulfurization media is generated within the system. High heat efficiency is maintained throughout the process, heat basically being derived from relatively low investment electrical resistance heating. Relatively low temperatures are employed which enable inexpensive materials of construction to be employed.

That which is sought to be protected is set forth in the following appended claims.

What is claimed is:

1. An improved method of treating sulfur-containing fluid coke which comprises the steps of: maintaining fluid coke particles in the form of a fluidized bed in a calcining zone, applying an electrical voltage across at least a portion of said bed, said voltage being of sufficient magnitude to maintain the temperature of said fluidized bed in the range of 1300 to 1900° F. due to the heat generated by the electrical resistance of said fluid coke particles, a hot gasiform stream of volatiles including hydrogen thus being liberated in said calcining zone, establishing a bed of fluid coke particles in a separate treating zone under a pressure between about 50 and 250 p.s.i.g., passing said hot gasiform stream liberated in said calcining zone upwardly through said treating zone, thus maintaining the particles

therein in the form of a fluidized bed at a temperature of about 1300 to 1500° F., the hydrogen in said gasiform stream serving to hydrodesulfurize said fluid coke particles in said treating zone.

2. The method of claim 1 wherein desulfurized fluid coke is withdrawn from said treating zone and passed to said calcining zone.

3. The method of claim 1 wherein calcined fluid coke is withdrawn from said calcining zone and passed to said treating zone.

4. The method of claim 1 wherein the gasiform stream liberated in said calcining zone contains at least 50 vol. percent hydrogen, and the fluid coke to be treated contains about 6.5 weight percent sulfur, said hydrogen reduces the sulfur content of the fluid coke in said treating zone to less than 3 wt. percent.

5. An improved process for improving the properties of fluid coke, said fluid coke having a sulfur content of more than 3 wt. percent and a real density of less than 1.7 gms./cc., which comprises, in combination, the steps of: maintaining fluid coke particles in the form of an electrically heated fluidized bed in a calcination zone, a sufficient voltage being applied across at least a portion of said bed so as to maintain said coke at a temperature of 1300 to 1900° F. due to the resistance heating of said fluid coke, said fluid coke thereby being calcined to a real density of at least 1.8 gms./cc. while yielding a hot stream of volatiles containing a substantial portion of hydrogen; passing said hot stream of volatiles to a desulfurization zone containing high sulfur content fluid coke, said liberated volatiles serving to maintain said fluid coke in the form of a fluidized bed at a temperature of 1300 to 1500° F. while hydrodesulfurizing said coke to yield a product of substantially less than 3 wt. percent sulfur.

6. The process of claim 5 wherein said low sulfur coke product withdrawn from said desulfurization zone is passed to said calcination zone.

7. The process of claim 5 wherein said volatiles liberated in said calcination zone contain at least 50 vol. percent hydrogen, and said desulfurization zone is maintained at a pressure of 50 to 250 p.s.i.g.

8. A process for improving the properties of fluid coke which has a sulfur content above about 3 wt. percent and a real density below about 1.7 g./cc. which comprises maintaining fluid coke particles as an electrically heated fluidized bed in a calcination zone by passing a sufficient voltage across at least a portion of said fluidized bed to maintain the coke particles at a temperature between about 1300° F. and 1900° F. by resistance heating of said fluid coke particles to calcine the coke particles to a real density of at least about 1.8 g./cc. while releasing volatile gaseous material containing a substantial portion of hydrogen, passing said volatile gaseous material directly to a desulfurization zone containing high sulfur content fluid coke to maintain said coke as a fluidized bed in said desulfurization zone at a temperature between about 1300° F. and 1500° F. to desulfurize said coke to less than about 3 wt. percent sulfur.

9. A process according to claim 8 wherein the gaseous stream leaving said hydrodesulfurization zone contains sulfurous gases, removing said sulfurous gases from said gaseous stream to recover a substantially sulfur free gaseous stream and passing said last-mentioned gaseous stream to the bottom of said calcination zone for upward passage therethrough as a fluidizing gas.

10. A method according to claim 3 wherein the gasiform stream leaving said treating zone contains sulfurous gases and the gasiform stream is treated to remove sulfurous gases and to leave a substantially sulfur free gasiform stream which is passed to the bottom of the said calcination zone for upward passage therethrough as a fluidizing gas.

11. A process according to claim 5 wherein calcined coke is withdrawn from said calcination zone and passed to said desulfurization zone.

12. A process for treating coke which comprises heating and calcining coke particles by the application of an electrical voltage to a fluidized bed of coke in a calcining zone maintained between about 1300° F. and 1900° F., separating hot hydrogen-containing gas from said fluidized coke particles and removing it from said calcining zone, maintaining a separate bed of green coke particles as a fluid bed in a desulfurization zone between about 1300° F. and 1500° F. and under a pressure between about 50 p.s.i.g. and 250 p.s.i.g., passing said separated hot hydrogen-containing gas upwardly through said desulfurization zone to fluidize and desulfurize the green coke particles therein and then passing the desulfurized coke particles to said calcining zone to be calcined.

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