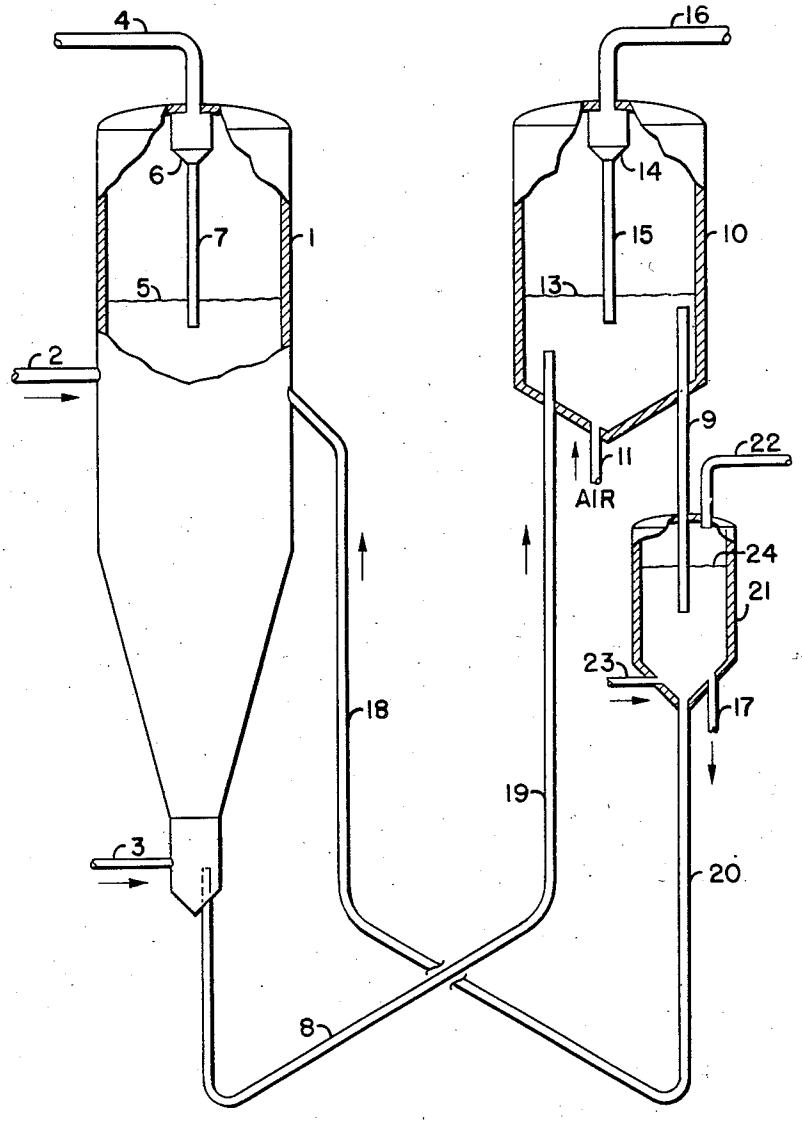
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INTEGRATED FLUID COKE DESULFURIZATION PROCESS

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INTEGRATED FLUID COKE DESULFURIZATION PROCESS

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This invention relates to improvements in the coking of heavy petroleum oils containing a high percentage of sulfur wherein the coking charge stock is contacted at coking temperatures with coke particles maintained in the form of a dense turbulent fluidized bed. More particularly, it relates to an integrated process of this nature wherein the sulfur is continuously removed from the circulating 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 heater or burner vessel. A stream of coke is transferred from the reactor to the burner vessel or heating zone employing a standpipe and riser system; air being supplied to the riser for conveying the solids to the burner. Sufficient coke or carbonaceous matter, or added fuel such as natural gas or torch oil 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, or an equivalent amount of other carbonaceous material such as fuel oil, natural gas, etc. 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 crudes, atmospheric and vacuum crude oil 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 D–180–52).

It is preferred to operate with solids having a particle size range of 75 to 1000 microns in diameter with a preferred average particle size 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 petroleum vacuum residua and pitches from highly asphaltic and sour crudes. Such residua frequently contain high concentrations of sulfur, i. e., 3 wt. percent or more, and the coke products 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 is about 2 times the sulfur content of the residuum 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 and preferably not over about 2 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.

The conventional methods of removing sulfur from coke from ordinary sources with gaseous reagents have, in general, not been too satisfactory. The results are even poorer when these procedures are applied to fluid coke. Delayed coke is more porous than fluid coke and the interstices are more connected and larger than in fluid coke. A treating gas consequently has relatively easy access to the sulfur. Fluid coke, on the other hand, is laminar in structure and may comprise some 30 to 100 superposed layers of coke. Thus, it is difficult for a reagent to penetrate more than a few outer layers. These difficulties of the fluid coke are even further compounded because of the beforementioned possibly higher than normal sulfur content of the coke derived from high sulfur petroleum feeds.

This invention provides an improved process for lowering the sulfur concentration of fluid coke by continuously removing the sulfur as it is laid down and before it becomes chemically more resistant to this removal and before it has been covered by succeeding layers of coke. The method comprises continuously contacting at least a portion of the hot circulating coke from the coke burning step with a gaseous sulfur removing reagent. The sulfur is thereby removed from the outer layer or layers from the coke particles as fast as it is laid down. The build up of the sulfur to high levels which are difficult to lower is thereby prevented.

The gaseous sulfur removing agents that can be utilized comprise those known in the art, such as steam, air, carbon dioxide, carbon monoxide, hydrogen, chlorine, coke oven gas, producer gas, ammonia and normally gaseous hydrocarbons such as methane. Hydrogen is preferred and can be utilized pure or in the form of hydroformer tail gas or other refinery streams. Sufficient hydrogen is used in order to provide a minimum hydrogen partial pressure of about 100 mm. Hg in the effluent gas from the treating zone. Preferably the hydrogen or other gas partial pressure is one atmosphere or higher. It is also preferred that the partial pressure of hydrogen sulfide in the effluent gas not exceed about 300 mm. Hg.

The conditions at which the gaseous reagents are utilized, are supplied in detail below. It should be emphasized, however, that these conditions are integrated

with the fluid coking process and represent an ideal manner of lowering the sulfur content.

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

In the drawing the numeral 1 is a coking vessel constructed of suitable materials for operation at 950° F. A bed of coke particles preheated to a sufficient temperature, e. g., 1150° F. to establish the required bed temperature of 950° F., is made up of suitable particles of 150–400 microns. The bed of solid particles reaches an upper level indicated by the numeral 5. The bed is fluidized by means of a gas such as steam at a temperature of 400° F. entering the vessel at the stripping portion via pipe 3. The fluidizing gas passes upwardly through the vessel at an average velocity at 1.5 ft./sec., when including the gas generated in the bed, establishing the solids at the indicated level. The fluidizing gas serves also to strip the vapors and gases from the coke which flows down through the vessel from pipe 20 as will be later related.

A reduced crude oil, containing 4.3 wt. percent sulfur, to be converted is preferably preheated to a temperature not above its cracking temperature, e. g., 700° F. It is introduced into the bed of hot coke particles via line 2, preferably at a plurality of points in the system. The oil upon contacting the hot particles undergoes decomposition and the vapors resulting therefrom assist in the fluidization of the solids in the bed and add to its general mobility and turbulent state. The product vapors pass upwardly through the bed and are removed from the coking vessel via line 4 after passing through cyclone 6 from which solids are returned to the bed via dipleg 7.

A stream of solid particles is removed from the coking vessel via line 8 and transported. A transfer line heater could be used as an alternative. Air is supplied via line 11 to burner 10. In the burner a portion of the carbonaceous materials, e. g., coke or materials deposited thereon, is burned to raise the temperature to a point sufficient to supply the heat to the endothermic reaction occurring in the coking vessel 1. The temperature of the burner solids is usually 100 to 300° F. higher than that of the solids in the coking vessel, e. g., 200° F. or actually 1150° F. in this example. The bed of coke is fluidized in vessel 10 in much the same manner as the bed in vessel 1. The solids are fluidized by the incoming air and resulting combustion gases and are maintained at a level indicated by the numeral 13. Hot flue gases pass through cyclone 14 and line 16. Any entrained solids are returned to the bed via dip-pipe 15. The hot circulating solids are continuously removed from burner 10 via line 9 to treating zone 21.

The circulating coke is fluidized by hydrogen tail gas from a hydroformer operation which enters through line 23. The temperature of the treating bed which has an upper level 24 is essentially that of the coke leaving the burner or 1150° F. A portion of the coke is removed from treating zone 21 through line 17 as product coke. Sulfur-containing gas, to fuel or to sulfur recovery, is withdrawn through line 22 and can be recirculated after treating. The residence time in treating zone 21 is about 10 minutes. About 200 standard cubic feet of hydrogen per ton of circulating coke are utilized in order to insure a minimum hydrogen partial pressure of 100 mm. Hg in the effluent; in this case 825 mm. in the effluent leaving through line 22. The hydrogen sulfide content of the effluent gas corresponds to a partial pressure of about 250 mm. Hg.

The desulfurized coke product withdrawn from line 17 can be calcined elsewhere if desired largely to increase the density and lower the volatile content. The remander of the coke in treating vessel 21 is recycled to the coker reactor through line 20 in order to maintain heat balance in the system. Fluidizing gas such as steam is introduced through line 18.

In another embodiment a portion of the circulating coke bypasses the treating zone. The residual portion is raised to a higher temperature in an auxiliary heating zone and this portion is then treated in the treating zone. The product coke is withdrawn and the remainder circulated back to the coker.

The burner and treater can be combined if desired in a single vessel. A series of superimposed beds of coke particles is set up therein. The burning is conducted in the upper beds and the treating with the sulfur removing gaseous agents in the lowermost beds as the coke particles descend.

The treatment with the gaseous reagent can also be in the form of a fixed or moving bed.

The following example further shows the advantage of this invention.

EXAMPLE

In an experiment coke was deposited on sand in the form of a superposed layer (I). Other coke particles were prepared in the conventional manner, i. e., built up entirely of coke (II). The diameter of both types of particles were the same and averaged about 300 microns. The sulfur content of the coke was also similar, 7 weight percent.

Both types of particles were treated with equivalent amounts of hydrogen under equivalent conditions at 1500° F. The sulfur content in the coke of I was reduced to 2.6 weight percent whereas the sulfur content of II was reduced to only 6.3 weight percent. This demonstrates the advantages of treating surface layers of coke as formed rather than permitting a relatively impervious barrier to be formed.

In order to express this information more fully the following conditions of operation of the various components including those in which the "fluid coke" is prepared are set forth below.

Conditions in fluid coker reactor 1

	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	0.5–1.5
Particle Size Range of Coke Particles, microns	75–1,000	150–400

Conditions in treating zone 21 (with hydrogen)

	Broad Range	Preferred Range
Temperature, °F	1,050–1,600	1,100–1,200.
Pressure, Atmospheres	1–5	2–4.
Coke Residence Time	5 mins.–10 hrs.	10–120 mins.
Exit Hydrogen Partial Pressure	100 mm. Hg–10 atm.	1.0–2 atm.

Conditions in burner 10

	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

The process of this invention is also applicable to the higher temperature coking for chemicals which conventionally is conducted at about 1150 to 1500° F. Under those circumstances the temperatures in the heating and treating zone are correspondingly raised.

The advantages of the process of this invention will be apparent to those skilled in the art. The sulfur content is maintained at acceptable levels by an integrated easily controlled process.

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. In a process for coking a heavy petroleum oil containing a high concentration of sulfur by the steps of contacting the 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; heating of the circulating coke particles removed from the coking zone in a separate heating zone to increase the temperature of said particles; returning of the circulating heated coke particles from the heating zone to the coking zone to supply heat thereto, and wherein the fluid coke product particles normally contain a high percentage of sulfur, the improvement which comprises continuously contacting of the hot circulating coke particles from the heating step to the coking step with a gaseous sulfur removing reagent at a temperature in the range of 1050° to 1600° F. whereby sulfur is continuously removed from the circulating coke particles and their sulfur content lowered.

2. The process of claim 1 in which the heavy petroleum oil contains at least 3 weight percent sulfur.

3. A process for coking a heavy petroleum oil containing a high concentration of sulfur which comprises the steps of contacting the 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 circulating coke particles removed from the coking zone in a burning zone to increase the particle temperature; contacting the circulating coke particles from the burning step while in the form of a dense turbulent fluidized bed in the treating zone with a gaseous sulfur removing reagent at a temperature in the range of 1050° to 1600° F. to continuously remove sulfur therefrom; withdrawing a portion of the treated coke as product and recirculating the remainder to the coking step.

4. The process of claim 3 in which the reagent is hydrogen.

5. The process of claim 4 in which maximum partial pressure of evolved hydrogen sulfide from the treating zone is 300 mm. Hg.

References Cited in the file of this patent

UNITED STATES PATENTS

2,595,366	Odell et al.	May 6, 1952
2,694,035	Smith et al.	Nov. 9, 1954