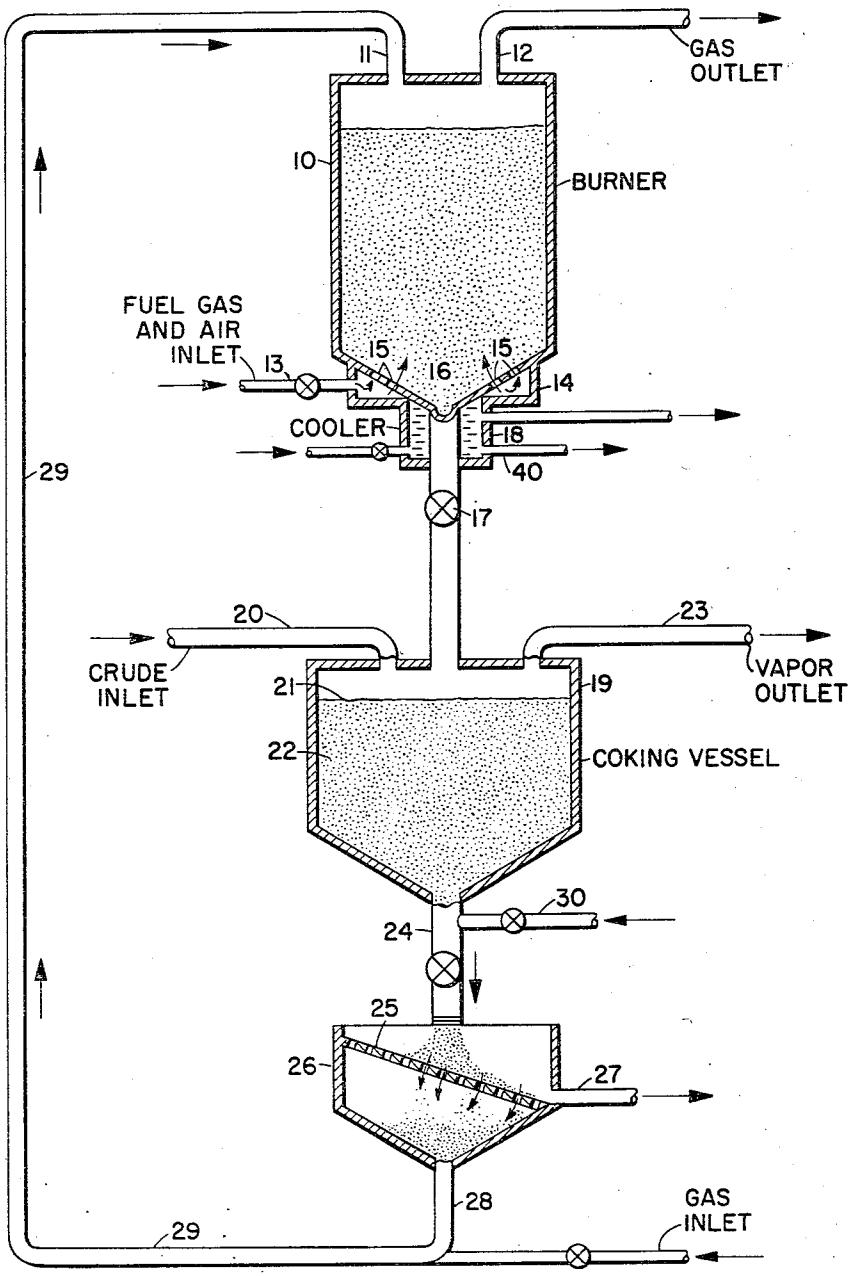
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PREPARATION AND DESULFURIZATION OF PETROLEUM COKE

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PREPARATION AND DESULFURIZATION OF PETROLEUM COKE

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4 Claims. (Cl. 202—14)

The present invention relates to improvements in the coking of heavy residual petroleum oils containing a high percentage of sulfur such as topped or reduced crude and is particularly concerned with a method for coking residual petroleum oils and for reducing the sulfur content of the resultant petroleum coke.

A related method of desulfurizing petroleum coke by sudden heating is described and claimed in jointly owned, copending application Serial No. 116,287, filed by W. G. Reed, Jr., concurrently with the present case.

This application is a continuation-in-part of Serial No. 116,364, filed September 17, 1949, now abandoned.

Crude petroleum oil is ordinarily subjected to distillation in order to remove distillable constituents boiling up to about 825° to 850° F. The residue or residual oil from this distillation operation or the so-called "reduced crude" which represents about 20–30 vol. percent of the original crude oil in a typical case is usually subjected to a pyrolytic treatment such as coking or visbreaking in order to obtain additional quantities of gas oil or petroleum fractions boiling within the range of from 400 to 850° F. which may be used as a charging stock to catalytic cracking systems to produce high quality motor fuels. The coking operation ordinarily involves preheating the residual oil to coking temperatures in a tube furnace or the like and then discharging the preheated oil into a coking retort or drum, preferably heat insulated, in which drum the oil undergoes conversion to form gas, gasoline, gas oil, and a solid residue of petroleum coke. In such an operation, the coke formed deposits as a solid clinging to the bottom and side walls of the drum. Eventually the operation must be discontinued and the coke removed by shutting down the drum, letting the coke dry and harden and then breaking the coke loose from the drum by mechanical or hydrauiic means.

There has also 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 rapid 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.

Heavy hydrocarbon oil feeds suitable for the 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–D–180–52.)

Such feeds frequently contain high concentrations of sulfur, i. e., 3 wt. percent or more, and the coke products produced from high sulfur feeds are also high in sulfur content. In general the sulfur content of the coke product from the 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 residue can thus range from 3 to 6 or even 8 wt. percent 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 and preferably 2 wt. percent sulfur is required. For example, low sulfur content coke is desired for the manufacture of phosphorus, 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.

It is the object of this invention to provide the art with a combined coking and desulfurization process which will produce petroleum coke of sufficiently low sulfur content to be suitable for these purposes.

It is a further object of this invention to prepare petroleum coke containing not more than 1 to 2 percent sulfur from high sulfur-containing petroleum residue.

These and other objects will appear more clearly from the detailed specification and claims which follow.

It has now been found that it is possible to reduce the sulfur content of petroleum coke by subjecting the same to a severe thermal treatment, i. e., a heat treatment of petroleum coke particles at temperatures of from 2500° to 3200° F. for periods of from 15 minutes to about 6 or 8 hours. In accordance with a preferred method of operation, preheated reduced crude is coked by discharging the oil onto the surface of desulfurized coke particles to lay down a thin layer of fresh coke on said particles which are then subjected to temperatures of 2500° to 3200° F. for a period sufficient to effect a substantial reduction in the sulfur content of the coke. In view of the fact that the layer of fresh coke deposited in this manner is very thin, the sulfur may readily diffuse to the surface and be driven off during a relatively short heating operation at said elevated temperatures.

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

Referring to the flow diagram, the numeral **10** is a desulfurizing vessel that is provided with an inlet **11** for coke particles and an outlet **12** for desulfurizing gases in its upper portion. An inlet **13** is connected to manifold **14** for the introduction of air or combustion gas into the bottom of desulfurizing vessel **10** through ports **15**. If desired, the combustion gas may be preheated by arranging a jacket around vessel **10** and placing the inlet near the upper part of the vessel so that the combustion gases are in contact with the outer wall of the vessel for a sufficient period to raise the temperature of said gases to the desired level before introducing the same into vessel **10**. Or, preferably, the combustion gases may be preheated by heat exchange with the effluent gas. The amount of air introduced into the vessel is sufficient to raise the temperature of the coke in at least a substantial portion of the vessel **10** to from 2500° to 2600° F. or 3200° F. In order to minimize combustion of the coke in attaining active desulfurizing temperatures an extraneous fuel such as natural gas or liquid fuel may be fired in order to supply part or all of the heat necessary

to effect desulfurization of the coke. Another oxygen-containing gas can be used instead of air.

Desulfurized coke is withdrawn from the bottom of vessel **10** through outlet pipe **16** which is provided with a flow control valve **17**. In order to reduce and control the temperatures of the coke withdrawn from vessel **10** to prevent damage to pipe **16** and valve **17** a cooling jacket **18** through which a suitable heat exchange fluid may be circulated is arranged around the outlet pipe **16**. A portion of the desulfurized coke may be withdrawn as product coke through line **40**.

Coke particles at temperatures of, say, e. g., 1500° to 2000° F. are discharged from outlet line **16** into the upper portion of coking drum **19**. Residual feed stock or reduced crude preheated to temperatures not above its cracking temperature, e. g., 800° to 850° F. is supplied through line **20** and sprayed upon the surface **21** of the bed of coke particles **22** in vessel **19**. If desired, rotatable distributing means may be arranged adjacent the outlet for conduit **16** in order to distribute the coke particles uniformly over the surface of the bed **22** and there may be associated with such distributor means suitable fixed or rotatable spray nozzles for distributing the preheated residual stock uniformly over the surface of the bed **22**. It is obviously necessary to achieve prompt quenching of the very hot incoming coke by the oil feed to prevent overcracking of the coking products as a consequence of prolonged contact with excessively hot coke. Either of these distributor means may also be provided with arms for rabbling the upper portion of the bed to prevent agglomeration of the coke particles. Vaporous reaction products from the coking operation are removed from the coking drum **19** through outlet pipe **23** and passed to suitable fractionating and recovery equipment (not shown).

The coke particles on which a thin layer of fresh or green coke has been deposited are withdrawn from the coking drum **19** through valve controlled outlet pipe **24** into which a small amount of sealing gas (flue gas) is introduced through line **30**, and are discharged onto screen **25** in vessel **26**. The screen serves to separate the coarse coke particles which may be withdrawn through outlet **27** while the undersized coke particles pass through the screen and are discharged from the bottom of vessel **26** through outlet **28** into transfer line **29** into which a suitable gas, flue gas, for example, may be introduced to convey the smaller coke particles to the inlet **11** of the desulfurizing vessel **10**. Instead of the gas or air lift for transferring the small coke particles from the bottom of vessel **26** to the top of the desulfurizing vessel **10** suitable mechanical means such as a bucket conveyor or the like could be used. Also it may be desirable to crush part of the coke by means not shown prior to recycling.

If the film of high sulfur coke on the particles removed by the above method is objectionable, fully treated coke may be withdrawn through line **40** as suggested above.

This method of desulfurizing is also applicable to coke prepared by the fluid coking process wherein the coke solids utilized have a particle diameter between 100 and 1000 microns, with an average of preferably 150 to 400 microns. Vigorous motion of the fluid bed is required to prevent agglomeration. This can be achieved, for example, by introducing the feed with some steam in the lower portion of the bed.

Fluid coke is laminar in structure and may comprise some 30 to 100 superposed layers of coke. Thus, it is difficult for a conventional desulfurizing reagent to penetrate more than a few outer layers.

The process of this invention desulfurizes the fluid coke in the high temperature heating step. The build up of the sulfur to high levels which are difficult to lower is thereby prevented as the coke is constantly deposited on prepurified coke, which also supplies heat to the bed.

The following examples are illustrative of the present invention:

EXAMPLE 1

Lump coke from the crude sources noted in the following table was held at about 2500° F. for several hours in a fixed bed furnace heated by combustion of part of the charge. Sulfur content was reduced as shown:

Table I

Crude from which Coke was Produced	Oficina		Lago			W. Texas	
Time at 2,500°F.—Hours	0	7	0	7	13	0	7
Sulfur in 1½" Lumps—Wt. Percent	3.0	1.9	4.0	1.3	0.8	5.0	1.2

In the above example sulfur was evolved from the entire lump of coke; sulfur reduction in a film of green coke laid down on the surface of a lump of low sulfur coke would be much more rapid.

EXAMPLE 2

The product distribution summarized in the following table may be expected from an 8% West Texas residuum when subjected to a continuous coking-coke desulfurization process, illustrated in the figure, at the conditions cited. The high coke still gasoline octane number obtained is associated with the high coking temperature used in this particular case; lower coking temperatures would result in lower gasoline octane number and a higher quality coke still bottoms. It will be noted that the rapid coking consequential to the high coking temperature that can be achieved by this procedure makes possible a very high oil throughput compared to more conventional coking processes.

Table II

Feed Stock	8% West Texas Residuum
Operating Conditions:	
Coke Desulfurization Zone—	
Coke Size—mesh	1-8.
Temperature, ° F	2,600.
Residence Time, minutes	15 or more.
Coking Zone—	
Preheat of Residuum, ° F	800.
Preheat of Coke, ° F	2,600.
Vapor Temperature in Drum, ° F	1,100.
Equilibrium Temp. of Coke, ° F	1,000.
Feed Rate of Residuum, vol. oil/vol. coking zone/hr	30.
Feed Rate of Coke, wt. coke/wt. oil	0.3 approx.
Product Distribution:	
Gasoline (10# RVP with UOP nonselective polymerization)	28 vol. percent (101 Oct. No.).
Coke Still Bottoms	17 vol. percent (−3° API).
Excess Butane	2 vol. percent.
Butane-Free Gas	23 wt. percent.
Ethylene	7 wt. percent.
Coke	33 wt. percent (1% S).

The foregoing description contains a limited number of embodiments of the present invention. It will be understood, however, that numerous variations are possible without departing from the scope of the following claims.

What is claimed is:

1. A method of preparing petroleum coke of low sulfur content which comprises the steps of maintaining a bed of coke particles of low sulfur content at a temperature of about 900° to 1100° F. in a coking zone; discharging a liquid, heavy petroleum oil coking charge stock, preheated to a temperature not above its cracking temperature and having a high concentration of sulfur onto such coke particles whereby the oil is converted to product vapors and thin layers of sulfur-containing green coke are deposited on the surface of the coke particles; heating the coke particles carrying said deposit of green coke thereon to a temperature in the range of 2500° to

3200° F.; maintaining the coke particles at temperatures within this range until the sulfur content of this layer of green coke is reduced to below 2 wt. percent; recovering a portion of the resulting desulfurized coke, and returning another portion of the hot desulfurized coke particles to the coking zone where they are rapidly cooled to coking temperature while supplying the heat necessary for coking the charge stock.

2. The process of claim 1 in which the thin layer of green coke deposited on the surface of the coke particles contains from 3 to 6 weight percent sulfur.

3. A method of preparing petroleum coke of low sulfur content which comprises maintaining a bed of coke particles of low sulfur content at temperatures of about 900° to 1100° F. in a coking zone, discharging reduced crude petroleum stock preheated to temperatures of about 800° to 850° F. onto such coke particles in order to form gas, gasoline and coke still bottoms and to deposit a thin layer of green coke containing from 3 to 6 weight percent of sulfur on the surface of said coke particles, heating the coke particles carrying said deposit of green coke thereon to temperatures of 2500° to 3200° F.; maintaining the coke particles at temperatures within this range until the sulfur content of this layer of green coke is reduced to below 2 weight percent, removing the desulfurized coke to a recovery point, recovering a portion of the resulting desulfurized coke, and returning another portion of the hot desulfurized coke particles to the coking zone where they are rapidly cooled to coking temperature while supplying the heat necessary for coking the reduced crude petroleum stock.

4. A process for making a petroleum coke of low sulfur content from heavy petroleum oil which comprises introducing petroleum coke particles of low sulfur content having a surface layer of green coke containing about

3 to 6 weight percent of sulfur to the top of a desulfurizing zone containing a bed of coke particles maintained at a desulfurizing temperature between about 2500° to 2600° F., also feeding a combustion gas composed of a mixture of air and extraneous fuel into a lower portion of the desulfurizing zone in an amount sufficient to maintain the bed of coke particles at the said desulfurizing temperature; passing the coke downwardly through the desulfurizing zone in the course of a period of about 15 minutes until the sulfur content of the coke is reduced to below about 1 percent; withdrawing flue gas from an upper part of the desulfurizing zone, also withdrawing a portion of the desulfurized coke particles from a lower part of the desulfurizing zone; cooling the withdrawn coke to a lower temperature between about 1500° to 2000° F.; passing the coke at the lower temperature into a coking zone; spraying preheated sulfur-containing heavy petroleum oil at a temperature of about 800° to 850° F. onto the coke particles in the coking zone at a rate of about one part of oil per 0.3 part of coke while quenching the coke to about 900° to 1100° F., thereby coating a layer of green coke containing about 3 to 6 weight percent of sulfur on the surface of the desulfurized coke particles, withdrawing the resulting volatile hydrocarbon products from the coking zone, also removing a portion of the coated coke particles from the coking zone, stripping and recovering volatile hydrocarbons from the removed coke particles, screening the stripped coke to separate coarse particles from smaller ones; recovering the coarse coke particles, mixing the separated smaller coke particles with a lift gas, and passing the resulting suspension to the top of the desulfurizing zone.

No references cited.