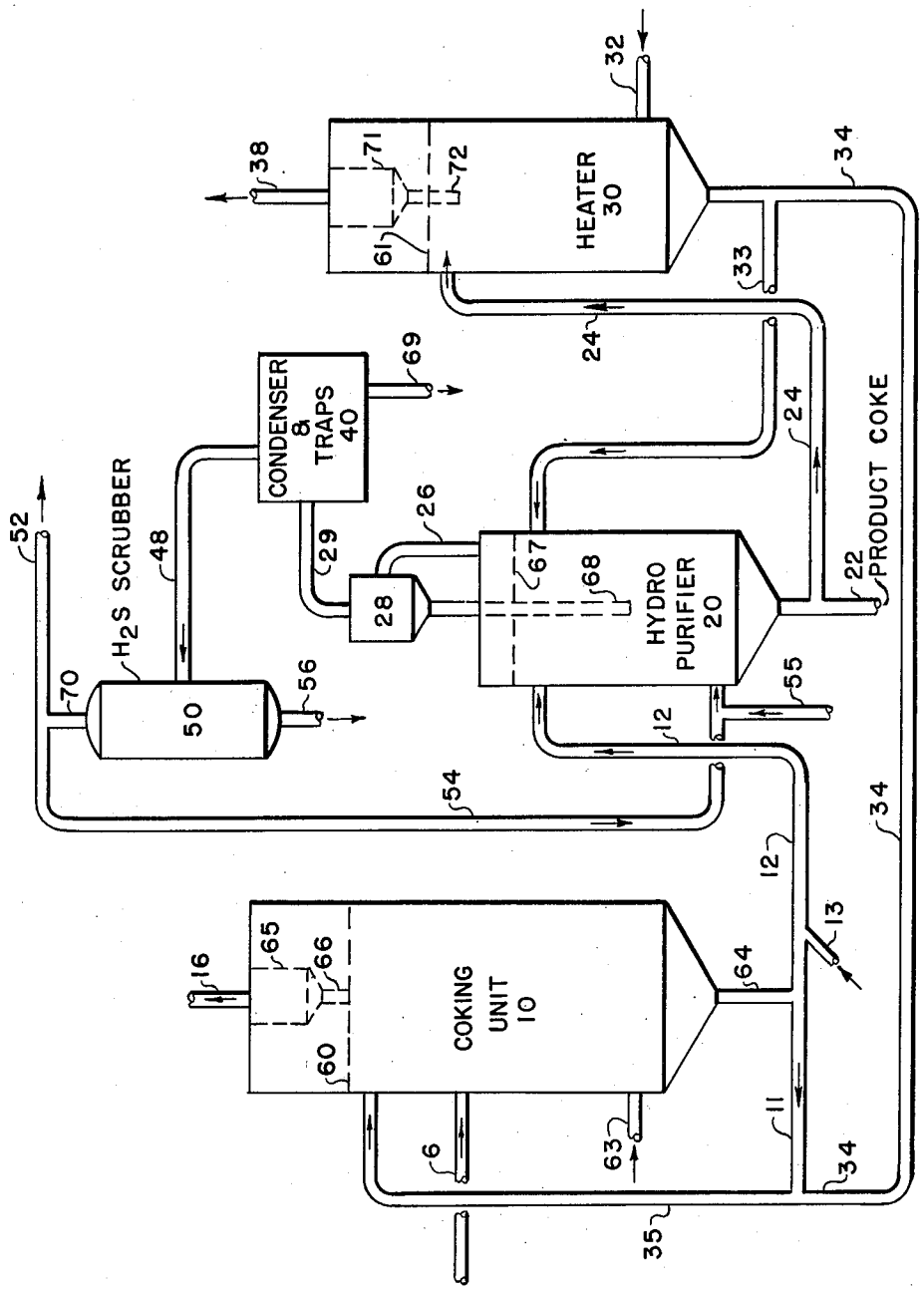
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INTEGRATED FLUID COKE DESULFURIZATION PROCESS

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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 and recovered.

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. Staged reactors can be employed. 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 process include 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 800° 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. %. (As to Conradson carbon residue see ASTM Test D–180–52.)

It is preferred to operate with solids having a 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 broardly 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 product 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 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 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 alkalies, 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, such as delayed coke, 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, however, 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 coke are even further compounded because of the before-mentioned possibly higher than normal sulfur content of the fluid coke derived from high sulfur petroleum feeds.

This invention provides an improved process for lowering the sulfur concentration of fluid coke which comprises removing the sulfur as fast as it is laid down and before it becomes chemically more resistant to this removal. The method involved continuously contacting at least a portion of the hot circulating coke going from the coking step to the heating step with hydrogen at elevated temperatures. 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 as the coke is constantly deposited on prepurified coke.

The hydrogen treating is conducted non-catalytically at a temperature of 1200° to 1400° F., preferably about 1300° F. At temperatures below about 1200° F. the rate of sulfur removal by hydrogen is extremely slow and requires an impractically long contact time. At temperatures higher than 1400° F. the rate of sulfur removal is also quite slow. The maximum rate of sulfur removal occurs at about 1300° F. The pressure in the hydrogen treating zone is approximately the same as that in the coking zone and may be in the range of about 0 to 25 pounds per square inch gage; hydrogen partial pressure may be in the range of one to three atmospheres absolute. The treating gas should contain at least 40% and normally comprises about 50 to 90% hydrogen with the remainder being, for the most part, methane and other

light hydrocarbon gases. The superficial gas velocity in the hydrogen treating zone is sufficient to maintain the coke in fluidized state; a velocity of 0.3 to 3.0 ft./sec., preferably 0.5 to 1.5 ft./sec., is contemplated. The contact time of the coke in the hydrogen treating zone is in the range of 1 to 20 minutes, preferably about 5 to 10 minutes. The hydrogen can be utilized pure or in the form of hydroformer tail gas or other refinery streams but is preferably treated in the conventional manner to remove hydrogen sulfide and other sulfur-containing compounds before use.

It should be emphasized that the conditions expressed are integrated with the fluid coking for fuels process and represent an ideal manner of lowering the sulfur content and recovering the sulfur in the form of useful compounds.

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

In the drawing numeral **10** represents a coking vessel constructed of suitable materials for operation at 1000° F. The temperature is maintained by the introduction of coke at about 1100° F. from line 35. A fluid bed of solid particles of 150 to 400 microns in diameter reaches an upper level indicated by numeral **60**. The bed is fluidized by means of a gas such as steam entering the vessel at a temperature of 400° F. via line **63**. The fluidizing gas passes upwardly through the vessel at an average velocity of 1.5 ft./sec., 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 **35**.

A reduced crude oil containing 3.5 weight percent sulfur to be converted, preferably preheated to a temperature not above its cracking temperature, e. g., 700° F., is introduced into the bed of hot coke particles via line **6**, 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 **16** after passing through cyclone **65** from which solids are returned to the bed via dipleg **66**. The coke formed is thus laid down in thin films on preheated coke as described hereafter. The coke stream is withdrawn through line **64** and exclusive of recycle through lines **11** and **35** is transported by means of hydrogen gas from line **13** to hydropurifier **20** through line **12**.

In purifier **20** the coke is maintained in a fluidized bed having an upper level **67** by means of hydrogen from lines **13**, **54** and **55**. The temperature of the coke in purifier **20** is 1300° F. and the residence time is 5 minutes. The upward superficial velocity of hydrogen in purifier **20** is 1.0 ft./sec. The hydrogen removes sulfur compounds and methane and a small amount of heavier hydrocarbons from the coke. The hot gases leaving the fluid bed pass through line **26** into cyclone **28** from which any entrained solids are returned to the bed via dipleg **68**. The gaseous materials are taken through line **29** to condenser and separator section **40** maintained at a temperature below about 100° F. where a small amount of condensable and tarry hydrocarbons are separated and removed through line **69**.

The residual gases comprising hydrogen, hydrogen sulfide, and gaseous hydrocarbons leave through line **48**, are taken to hydrogen sulfide scrubber **50** containing triethanolamine. The scrubber solution removes the hydrogen sulfide and itself can be removed through line **56** where it can be degassed and recycled. The cooled hydrogen sulfide can be compressed and sold or used for commercial enterprises.

Other conventional means of separating hydrogen sulfide from hydrogen such as water scrubbing, caustic soda scrubbing, sodium phenolate scrubbing, tripotassium phosphate scrubbing, or the like, can be employed. The hydrogen is taken overhead through line **70** and recycled through line **54** as previously described. Any venting and purging is done through line **52**. Make up hydrogen is added through line **55**.

The purified coke from hydropurifier **20** is withdrawn through line **22**. A portion of the coke from the purifier is fed by means of line **24** to heater **30**. Air is supplied via line **32** to heater **30**. In the heater a portion of the carbonaceous materials, e. g., coke or materials deposited thereon, is burned to raise the temperature to a point sufficient to keep the system in heat balance, in this case to about 1500° F. The bed of coke in vessel 30 is fluidized to a bed level **61** in much the same manner as the bed in vessel **10**. Other gases or liquid fuels can be substituted in all or part for the coke burned. Similarly a transfer line burner system could be employed. Hot flue gases pass through cyclone **71** and line **38** with entrained solids being returned to the bed via dipleg **72**. A portion of the heated coke is withdrawn through line **33** and passed to hydropurifier **20** as a source of heat. To obtain a temperature of 1300° F. in purifier **20**, 1½ parts of stream **33** at 1500° F. is required for 1 part of coke from line **12** at 1000° F. These ratios can be varied according to temperature requirements and heat losses in the transfer lines. The other portion of the coke stream is passed through line **34** to the coking unit.

The coke in line **34** at a temperature of 1500° F. is mixed with 1000° F. coke withdrawn from the reactor **10** by lines **64** and **11** and the mixture at a temperature of about 1100° F. is introduced into reactor **10** by line **35** as hereinbefore described.

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

CONDITIONS IN FLUID COKER REACTOR 10

	Broad Range	Preferred Range
Temperature, °F	900–1,500	950–1,050
Pressure, p. s. i. g	0–100	5–25
Superficial Velocity of Fluidizing Gas, Ft./sec.	0.3–5.0	1.5–3.0
Average Size of Coke Particles, microns	50–1,000	100–400

CONDITIONS IN TREATING ZONE 20

	Broad Range	Preferred Range
Temperature, °F	1,200–1,400	1,250–1,350
Pressure, p. s. i. g	0–100	5–25
Hydrogen Partial Pressure, Atmospheres Absolute	0.5–7	1–3
Superficial Gas Velocity, Ft./sec	0.3–3.0	0.5–1.5
Coke Residence Time, Min	1–20	5–10

CONDITIONS IN HEATER 30

	Broad Range	Preferred Range
Temperature, °F	1,250–1,600	1,400–1,500
Superficial Velocity of Fluidizing Gas, Ft./sec	0.3–3.0	1.0–1.5

The process of this invention is also applicable to the coking of heavy hydrocarbon oils for the production of chemicals, e. g., principally unsaturated hydrocarbons. A process of this nature is conducted with reactor temperatures of about 1200° to 1500° F. and heater temperatures of 1300° F. to 1600° F. Transfer line systems are preferred for both of these steps in the coking at high temperature for chemicals.

The value of treating coke in thin layers and the effect of temperature of treating are shown by the following data treating 100 to 400 micron particles with hydrogen at 1500 v./v./hr. In one case solid particles of high sulfur (7%) coke were treated. In the other case the

coke was deposited in a thin layer (1 to 2 microns thick) on sand:

Temperature, °F.	Initial rate of Sulfur Removal, Lbs. of Sulfur per Ton of Coke per Minute	
	Solid Coke	Thin Layer of Coke
1,000	0.3	3
1,200	1.2	13
1,300	2.0	21.5
1,400	1.4	15
1,600	1.3	14

Experience has shown that initial desulfurization rates are not maintained when the total particle is to be purified and the rate drops off tremendously after the outside layers have been desulfurized. The differences between the total particle and thin film after allowance for this decrease in rate are as follows:

	Solid Particle	Thin Layer
Time on H_2 at 1,300° F. to Reduce Sulfur to 2%---	12 hours---	5 min.

Thus the operability of the process is demonstrated.

The advantages of this invention will be apparent to those skilled in the art. Improved purification is obtained in an integrated system in that the coke is treated before it is rendered passive by excessive temperatures in the burner section. The coke is thus deposited in thin layers on prepurified coke. The loss of some of the sulfur compounds in the burner is avoided by purifying prior to the excessive burner heating. This process works best with freshly deposited films of coke on prepurified coke as a nucleus. The purification of the coke prior to the burner section concentrates all the sulfur available as hydrogen sulfide. In addition to this gain in sulfur compounds a relatively pure coke passes to the burner which minimizes the objectionable air contamination from sulfur dioxide which otherwise would be encountered.

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 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 dense, turbulent, fluidized bed of coke particles maintained in a coking 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; withdrawing the coke particles from the coking zone; contacting the hot circulating coke with hydrogen in a treating zone at a temperature in the range of 1200 to 1400° F. to remove sulfur therefrom; heating a portion of the hydrogen treated circulating coke particles removed from the coking zone in a separate heating zone to increase the temperature of said particles and returning a portion of the circulating heated coke particles from the heating zone to the coking zone to supply heat thereto.

2. The process of claim 1 including the additional step of withdrawing product coke from the hydrogen treating zone.

3. The process of claim 2 including the additional step of returning a portion of the circulating heated coke particles from the heating zone to the hydrogen treating zone to supply heat thereto.

4. The process of claim 3 including the additional step of recovering hydrogen sulfide from the overhead hydrogen containing gases from the hydrogen treating zone and recycling the hydrogen from the overhead gases to the hydrogen contacting step.

5. The process of claim 1 in which the hydrogen contacting step is carried out while the coke is maintained in the form of a dense turbulent fluidized bed.

6. The process of claim 5 in which the hydrogen contacting step is carried out for a period of time in the range of 1–20 minutes.

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