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DESULFURIZATION OF FLUID COKE WITH HYDROGEN ABOVE 2400° F.

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This invention relates to improvements in desulfurizing and increasing the density of coke particles containing high percentages of sulfur. More particularly it relates to an efficient high yield desulfurization of petroleum coke particles from the fluid coking process by subjecting the coke particles to treatment at elevated temperatures with a gas consisting essentially of hydrogen whereby the sulfur content of the coke is reduced and its density increased.

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 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. A transfer line or staged reactors can be employed. 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 are 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, usually but not necessarily separate. A stream of coke is transferred from the reactor to the burner vessel, such as a transfer line or fluid bed burner, employing a standpipe and riser system; air being supplied to the riser for conveying the solids to the burner. Sufficient coke or other carbonaceous matter is burned in the burning vessel with an oxygen-containing gas 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 the coke, based on the feed, is normally 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 partially recycled to the reactor, the remainder being withdrawn.

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-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 withdrawn product coke has a diameter predominantly in the range of about 20 to 80 mesh, i. e., about 60 to 90 wt. percent.

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 heavy petroleum oils, i. e., 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 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 residue can range from 5 to 8 weight percent sulfur or more.

The high sulfur content of the coke product poses a major problem in its efficient utilization. For most nonfuel or premium fuel uses a low sulfur content coke, about or below 3 wt. percent sulfur is required and in some cases 2% or less. 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 applications, for the production of electrode carbon for various electrochemical applications such as the manufacture of aluminum and the like.

In addition the real density of the fluid coke is about 1.5 which is below the minimum figure of about 1.8 required for many specialty applications. The increasing of the density and the lowering of the sulfur and volatile content is particularly necessary before the fluid coke is suitable for manufacture into electrodes, one of the major uses of petroleum coke.

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 compared to delayed coke. A treating gas has relatively difficult access to the sulfur in fluid coke compared to delayed coke since fluid coke is laminar in structure and may comprise some 30 to 100 superposed layers of coke. Thus, it is difficult for a reagent such as a treating gas to penetrate more than a few outer layers. These difficulties associated with the treatment 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 and increasing its density. The process comprises subjecting the high sulfur containing fluid coke to treatment at controlled elevated temperatures with a gas consisting essentially of hydrogen whereby the sulfur content of coke is reduced and its real density increased.

It is surprising to find that hydrogen should be so far superior to other commercially available gases utilized for the same purpose under the same conditions. Thus, for example, as explained in further detail below, air, steam, carbon dioxide and nitrogen have been found to be less effective in terms of both yield and desulfurization. The term "gas consisting essentially of hydro-

gen" is to be understood as restricting the gas to hydrogen, i. e., a minimum of about 85 vol. percent, with or without the presence of the usual impurities and minor non-interfering components such as, e. g., 10 vol. percent CH_4 and 5 vol. percent higher paraffin gases. The hydrogen is utilized in an amount of 50 to 5000 v./v./hr. (volume of gas per volume of coke per hour), preferably 100 to 2000 v./v./hr.

The temperature utilized is a minimum of 2400° F. Inferior results are obtained below this temperature within practicable time limits. It is preferred to utilize a temperature in the range of 2400° to 2800° F. These temperatures can be achieved preferably by direct heat transfer with hot solids, e. g. coke, pebbles or shot. Indirect heat transfer such as from the combustion of natural gas can also be employed. The pressure is near atmospheric, i. e., not higher than about 100 lbs.

The time interval utilized depends on the temperature and pressure but is in the range of 15 minutes to 10 hours. The higher the temperature the lower the time interval. For example, 15 minutes can be sufficient at 2700° F., whereas 3 hours can be required at 2400° F.

Treatment of the fluid coke can be conducted while the latter is in the form of a dense, turbulent fluidized bed, a moving bed or a fixed bed, usually depending on the equipment available.

When the desulfurization is carried out in the fluidized solids technique it is especially desirable to recirculate all or a portion of the effluent gas after scrubbing out H_2S so as to effect better utilization of the hydrogen, to conserve heat, and to cut down on the gas requirements.

The following examples illustrate the advantages of this invention.

EXAMPLE 1

In one series of runs the temperature of calcination was varied from 1350° F. to 2700° F. while using a gas consisting essentially of hydrogen as the treating gas. The coke was fluidized for 30 minutes with hydrogen at each temperature as shown in Table I.

Table I

HYDROGEN CALCINATION OF FLUID COKE [a]; EFFECT OF TEMPERATURE; 30-MINUTE TREATMENT

Temp., °F.	Coke Yield, Wt. percent	Sulfur, Wt. percent	Real Density, 25° C.
1,350	95	5.9	1.53
1,800	95	6.7	1.81
2,100	92	6.5	1.87
2,400	89	4.9	1.87
2,700	83	1.8	1.86

[a] Original green coke contained 7.5 wt. percent sulfur and had a density of 1.50 at 25° C.

It is apparent from the data in Table I that temperatures of 2400° F. and above are required to get a good rate of sulfur removal.

EXAMPLE 2

Direct comparisons were made between gases consisting essentially of hydrogen and several other common gases in fluid coke calcining at 2400° and 2700° F. The coke was fluidized for 30 minutes with the various gases, all at the same v./v./hr. Summary data are given in Table II.

Table II

COMPARISON OF HYDROGEN WITH OTHER COMMON GASES IN FLUID COKE CALCINING (30-MINUTE TREATMENT) [a]

Treating Gas	H_2	H_2	N_2	N_2	Air	Air	Steam	CO	CO_2	CH_4	Steam (75 vol. Percent) CO (25 vol. Percent)
Temperature, ° F	2,400	2,700	2,400	2,700	2,400	2,700	2,400	2,400	2,400	2,400	2,400
Coke Yield, Wt., Percent	89	83	92	85	(b)	(b)	(b)	90	80	[c] 97	80
Sulfur, Wt., Percent	4.9	1.8	7.4	3.7	6.7	2.8	5.2	6.2	5.8	5.6	5.7

[a] Original green coke contained 7.5 wt. percent sulfur.
[b] Yields not available for these runs.
[c] Yield high because of carbon deposition from CH_4 cracking.

Hydrogen gives high coke yields for a given reduction in sulfur content. Although yield values are not shown in Table II for air and steam, these gases are known to consume coke rapidly at these temperatures. This fact is more apparent at longer contact times.

Yields are lower for air and steam because both attack the carbon. Oxygen in the air burns the coke to give CO and steam gives $CO+H_2$ by the water gas reaction.

As an illustration, one run made with air at 4500 v./v./hr. at 2400° F. and for a time of 20 minutes gave a yield of 82.5% as compared with 89% for hydrogen at a time of 30 minutes.

Another air run made at 2700° F. gave a yield of only 74.0% using a 20 minute time of treating.

It is important to note the advantage for hydrogen over all the other gases shown in sulfur content of the coke product. This holds for both 2400° F. and 2700° F. The superiority for hydrogen over nitrogen is significant in view of the fact that both are inert gases insofar as any reaction with the coke is concerned.

Analyses of exhaust gases from hydrogen and nitrogen calcining have been of special interest. Although hydrogen has given more efficient sulfur removal than nitrogen, the exhaust gases from both contain carbon disulfide as the main sulfur-bearing compound. This result is unexpected, since an entirely different mechanism might be anticipated for the hydrogen. For example, one should expect to get mostly hydrogen sulfide with the use of hydrogen.

These runs were discontinued for the most part after 30 minutes because time intervals of that nature have been found to be valid and reliable in screening tests on different gaseous materials. Varying the temperature or time of treatment or both within the prescribed ranges can bring the sulfur content down to the levels required.

The conditions usually encountered in a fluid coker for fuels are also listed below so as to further illustrate how the coke was prepared. Higher temperatures are utilized in coking for chemicals.

CONDITIONS IN FLUID COKER REACTOR

	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.	0.2–10	0.5–4
Feed Rate (Solids/Oil Ratio)	2–30	7–15

The advantages of the process of this invention will be apparent to those skilled in the art. The sulfur con-

tent is reduced to acceptable levels by an easily controlled economical process and satisfactory yields are maintained.

Several cycles of treatment with 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 to a maximum sulfur content of 3 weight % and increasing the density of fluid coke particles containing a high percentage of sulfur, a minimum of about 5 weight %, said particles having been produced by contacting a heavy petroleum oil coking charge stock at a coking temperature with a body of fluidized coke particles 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 a portion of the coke particles from the coking zone in a heating zone to increase the temperature of said fluidized particles, returning a portion of the heated

coke particles from the heating zone to the coking zone and withdrawing product particles which comprises the step of contacting at about atmospheric pressure the product coke particles with about 100 to 2000 v/v/hr. of a gas consisting essentially, at least 85 volume % of hydrogen at a minimum temperature of 2400° F. for a treating time in the range of about 15 minutes to 3 hours.

2. The process of claim 1 in which the contacting of the hydrogen containing gas is conducted at a temperature in the range of 2400° F. to 2800° F.

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