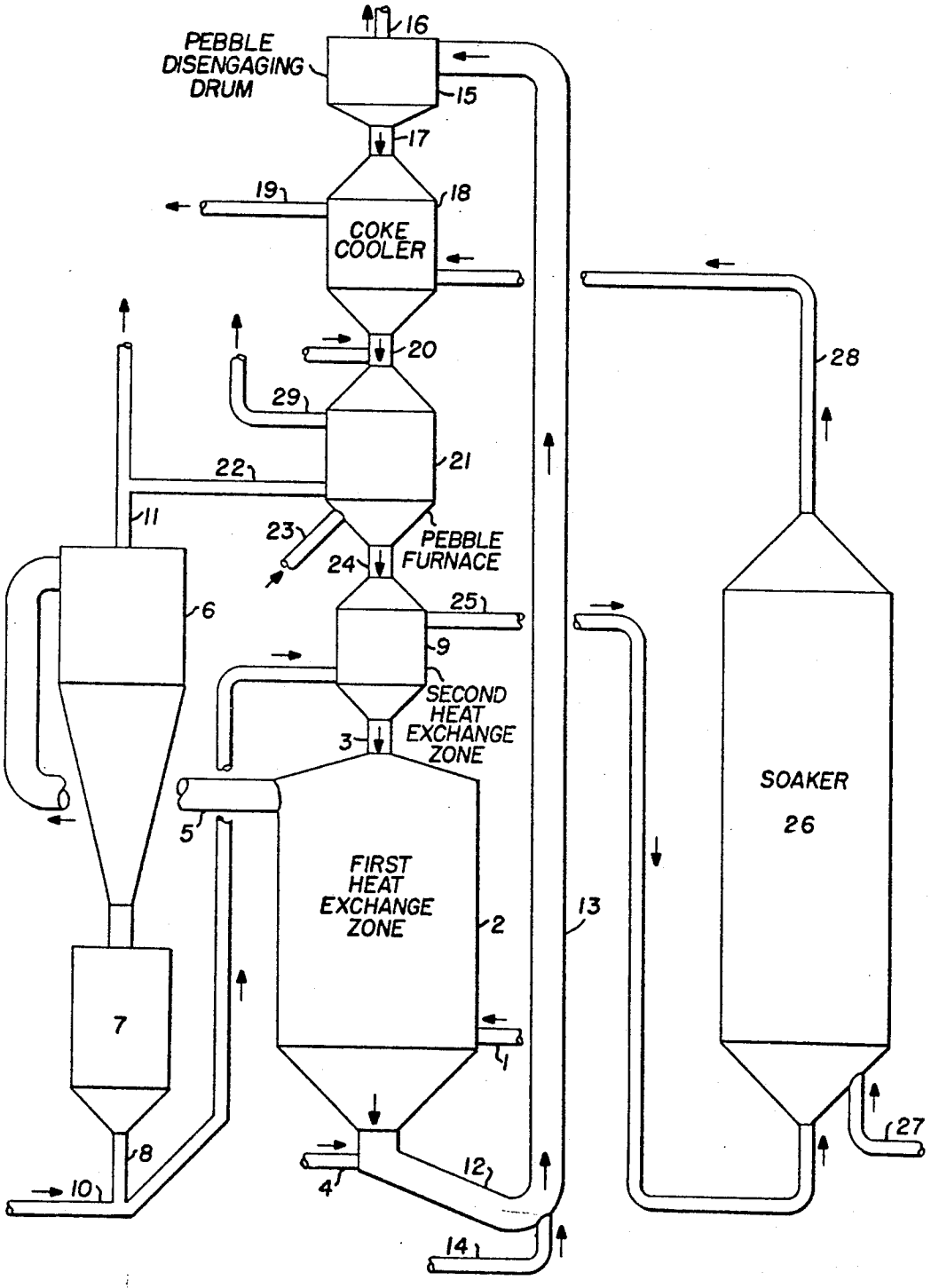
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RECOVERY OF PRODUCT VAPORS FROM FLUID COKE

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RECOVERY OF PRODUCT VAPORS FROM FLUID COKE

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This invention relates to improvements in calcining fluid coke. More particularly it relates to the staged calcining of fluid coke at increasing temperatures wherein the volatile products contained therein and the sulfur-containing products are separately recovered. In a more specific embodiment it provides an improved process using a modified feed-to-product pebble heat exchanger system.

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. Transfer line or fluid bed reactors and burners can be used. 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. 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 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, usually but not necessarily separate. A stream of coke is thus 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 added 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 net coke production, which represents the coke made less the coke burned, is withdrawn.

Heavy hydrocarbon oil feeds suitable for the coking process include heavy crudes, atmospheric and crude vacuum bottoms, pitch, asphalt, other heavy hydrocarbon petroluem 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.)

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.

The fluid coke product particles have a particle diameter predominantly, i. e., about 60 to 90 wt. percent in the range of 20 to 80 mesh, a sulfur content in many cases above 6 wt. percent, and a volatile content of 2 to 10 wt. percent. They have a real density of about 1.4 to 1.7 which is too low for use in the manufacture of carbon electrodes for making aluminum and other purposes. Increased density, lower sulfur and volatile contents are particularly necessary before the fluid coke is suitable for manufacture into these electrodes, one of the major uses of petroleum coke. These objectives are obtained by calcination at minimum temperatures of 2100° F. or even 2400° F. or higher. This high temperature treatment is expensive. It is consequently advantageous to increase the recovery of valuable products therefrom and to improve the efficiency of the process.

This invention provides an improved process for calcining fluid coke. The process comprises heating the coke in two stages of increasing temperature so that separate relatively concentrated vaporous streams of the volatile products and the sulfur-containing products are recovered.

The heating in the first stage is conducted at a temperature in the range of 1600° to 2400° F. and preferably 1800° to 2200° F. for a period of time in the range of 0.1 to 30 minutes. The volatile products comprise principally hydrogen and methane and are substantially free of sulfur-containing materials, i. e., less than 10 percent of the total sulfur on the coke. These volatile products are thus withdrawn as a separate stream. The heating in the first stage can be done directly or indirectly while the fluid coke is in the form of a moving bed, a fluid bed, or a dispersed suspension including a high velocity confined stream in a transfer line. A typical composition of the recovered volatile products is: 49 mol. percent H_2, 49 mol. percent CH_4, the remainder CO and CO_2 with traces of C_2s and C_3s.

The thus devolatilized, heated fluid coke is then subjected to an additional stage of heating and soaking, i. e., at a higher temperature in the range of 2300° to 2700° F. and preferably 2400° to 2600° F. for a period of time from 0.5 to 10 hours. The heating can be done directly or indirectly. A separate stream of vaporous sulfur containing products is withdrawn from this second stage. A typical composition of the recovered sulfur containing products which contain principally CS_2 are:

CS_2	49 mol. percent.
S_2	8 mol. percent.
CO	14 mol. percent.
N_2	28 mol. percent.
Remainder	CO_2+COS (carbonyl sulfide).

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

The hot feed coke, e. g., coke from the fluid coke burner at a temperature of 1125° F. is sent through line 1 to the bottom portion of a first heat exchange zone 2. The temperature of the coke is raised to 1800° F. by the column of hot pebbles which gravitates downward from throat 3 and countercurrently contacts the upflowing coke particles which are in the form of a dispersed suspension. The superficial velocity of the coke particles is in the range of 0.1 to 1.0 ft./sec., e. g., 0.2 ft./sec. The evolved volatiles from the fluid coke supply a substantial portion of the required entraining gas. Small amounts of stripping gas supply the additional entraining gas requirements through line 4. Stripping gases that can be used include hydrogen, methane, steam and other gases consistent with the purpose of the end volatiles. The coke is thus maintained in heat exchange zone 2 for about 10 seconds. This is sufficient to remove substantially all the volatile matter from the coke. The volatile matter

together with entrained coke is removed through line 5 into the vapor solids separating cyclone 6. The hot coke falls into collection hopper 7 and is then sent through line 8 to second heat exchange zone 9. Small amounts of lift gas, preferably an inert gas such as nitrogen or flue gas accomplishes this through line 10. The volatiles, whose composition is comprised largely of hydrogen and methane as explained before, leave the cyclone 6 through line 11.

The pebbles withdrawn from heat exchange zone 2 through line 12 at a temperature of 1175° F. are transported by an inert lift gas from line 14 through line 13 to pebble disengaging drum 15. The lift gases are vented through line 16. Pebbles gravitate downward from drum 15 through throat 17 to coke cooler 18. The coke enters coke cooler 18 at a temperature of 2700° F. where it countercurrently contacts the cooler pebbles. The coke and vaporous sulfur-containing materials cooled to a temperature of 1225° F. are taken off through line 19 and sent to product recovery, not shown, where the thus calcined coke is separated from the other products such as carbon disulfide. The latter in turn can be separated from the other vaporous materials by means known in the art. The pebbles which have thus been heated to e. g. 2150° F. gravitate through throat 20 into pebble furnace 21.

The temperature of the pebbles is raised to 2830° F. by the combustion of any available combustible components, e. g., natural gas, torch oil, etc., and flue gases are withdrawn through line 29. If desired a portion of the volatile matter can be utilized for combustion through line 22. Air supports the combustion through line 23.

The thus heated pebbles gravitate through throat 24 into second heat exchange zone 9. It thus countercurrently contacts the upflowing dispersed suspension of coke at 1800° F. The coke residence time in heat exchange zone 9 itself is the same order of magnitude as the first heat exchange zone, e. g., about 10 seconds and is heated to e. g. 2700° F. The pebbles cooled to e. g. 1900° F. gravitate through throat 3 to first heat exchange zone 2 as pointed out previously. The heated coke at a temperature of 2700° F. is entrained through line 25 to soaker 26. It is maintained in this soaking zone in the form of an upflow moving bed for a time interval in the range of ½ hour to 10 hours, e. g., 1 hour. The upflowing moving bed is maintained by a fluidizing gas through line 27 at a superficial velocity of .2 ft./sec. The fluidizing gas is kept at a minimum so as not to dilute the product. The evolved sulfurous vapors contribute toward the moving of the bed. The effluent from line 28 contains entrained coke, the inert fluidizing gases and evolved sulfurous vapors including principally carbon disulfide. This effluent is sent to coke cooler 18 from which it is processed as described above.

Solid inert heat exchange materials which may be utilized in the pebble heater system of this invention are generally termed "pebbles." The term "pebbles" as used herein denotes any substantially solid, inert material of flowable size and form which has sufficient strength to withstand mechanical pressures and the temperatures encountered within the pebble heater system. These pebbles must be of such structure that they can carry large amounts of heat from one chamber to another without rapid deterioration or substantial breakage. Pebbles which may be satisfactorily used in this treating system may be substantially spherical in shape and range from about one-eighth inch to about one inch in diameter. The pebbles are preferably of a size within the range of from one-eighth inch to five-eighths inch in diameter and have a greater free fall velocity than the coke. Materials which may be used singly or in combination in the formation of such pebbles include among others alumina, silicon carbide, periclase, beryllia, mullite, magnesia, and silica. It is preferred that the pebbles be very porous, similar in structure to a sponge.

The advantages of this invention are shown in the following example.

EXAMPLE

The figures presented below are based on different calcination systems and the use of different fluidizing gases. Case I represents single stage calcination at a temperature of 2780° F. with H_2 as the fluidizing gas. Cases II, III, and IV are staged calcinations according to the process of this invention utilizing a temperature of 2780° F. in the second stage and H_2, N_2 and flue gas as the respective fluidizing gases. In all cases equivalent amounts of fluidizing gas are employed. The compositions of evolved gases are presented below:

Case	I	II	III	IV
CS_2	3.5	50.6	52.3	48.4
H_2S	7.7	10.1	.....	0.3
COS	.....	.....	.....	0.2
S_2	0.6	8.6	8.9	8.1
N_2	.....	.....	38.8	27.2
H_2	88.2	30.7	.....	1.0
CO	.....	.....	.....	14.8
CO_2	.....	.....	.....	.....

It is apparent how the yield of CS_2 is increased at least about fifteen fold by the process of this invention as compared to a single stage operation.

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

Conditions in fluid coker reaction

	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 this invention will be apparent to the skilled in the art.

The heat requirements are reduced since the volatile matter is removed before it has a chance to crack. This saves the heat of cracking and the heat required to raise the gas temperature from about 1800° F. to desulfurization temperature.

The sulfur-rich gases leaving the system are much smaller in volume since they are not mixed with the volatile matter. Therefore, the sulfur recovery problem is simplified.

Since the volatile matter is not contaminated with sulfur, it can be used directly as fuel or can be cracked to form hydrogen. If economic studies show that the gas has no value, it can be vented without polluting the atmosphere with sulfur.

Because the volatile matter is removed early in the process, the soaker, coke cooler, solids recovery system and piping can be made smaller in size. The volatiles evolved also form a substantial part of the entraining gas. In addition, it has been found that if the sulfur stream is not brought in contact with the hydrogen-rich volatile matter, most of the sulfur is removed as carbon disulfide. In the presence of hydrogen the sulfur will tend to form hydrogen sulfide, thus cutting down on the yield of the more desirable carbon disulfide. Thus in the process of this invention CS_2 can be substantially the only sulfur containing gas produced.

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 and increasing the density of fluid coke particles containing a high percentage of sulfur, and recovering valuable products, said fluid coke

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 coke product particles which comprises the steps of maintaining the coke particles at a temperature in the range of 1600° to 2400° F. for a period of time of from 0.1 to 30 minutes; withdrawing a relatively concentrated vaporous stream of substantially all the volatile products on the coke and comprising principally hydrogen and methane, substantially free of sulfur containing products; maintaining the thus treated coke particles at a higher temperature in the range of 2300° to 2700° F. for a period of time in the range of 0.5 to 10 hours, and withdrawing evolved sulfur containing products as a relatively concentrated vaporous stream.

2. The process of claim 1 in which the sulfur containing vaporous stream comprises principally carbon disulfide.

3. A staged process for devolatilizing and desulfurizing fluid coke particles and recovering valuable products therefrom which comprises the steps of heating in a first heat exchange zone the coke particles to a temperature in the range of about 1600° to 2400° F. for a period of time of from 0.1 to 30 minutes by countercurrently contacting them with gravitating hot pebbles to remove substantially all the volatile products, substantially free of sulfur containing products, from the coke; separating the vaporous volatile products and by entrainment, the coke from the pebbles; separating the coke from the vaporous volatile products; heating the thus separated coke particles in a second heat exchange zone to an elevated temperature in the range of about 2300° to 2700° F. by countercurrently contacting them with gravitating hot pebbles; separating by entrainment the hot coke particles from the pebbles and sending the coke to a soaking zone where it is maintained at a temperature in the range of about 2300° to 2700° F. for a period of time in the range of 0.5 to 10 hours so as to evolve vaporous, sulfur-containing products; removing an effluent of entrained coke and sulfur-containing products from the soaking zone to a cooling zone; cooling the effluent in the cooling zone by countercurrently contacting it with cooler gravitating pebbles from the first heat exchange zone; separating by entrainment the effluent from the gravitating pebbles; separating the resultant product coke from the vaporous sulfur-containing products; raising the temperature of the pebbles from the cooling zone by combustion in a combustion zone and gravitating the thus heated pebbles to the second heat exchange zone.

4. The process of claim 3 in which the coke particles in the first and second heat exchange zones are in the form of a dispersed suspension.

5. The process of claim 4 in which the evolved volatile products in the first heat exchange zone provide a substantial part of the required entrainment.

6. The process of claim 5 in which the coke particles in the soaking zone are in the form of an upflowing moving bed.

7. The process of claim 3 including the additional step of sending evolved volatile products from the first heat exchange zone to the combustion zone for combustion therein.

8. The process of claim 3 in which the evolved volatile products in the first heat exchange zone comprise principally hydrogen and methane.

9. The process of claim 3 in which the sulfur-containing vaporous products comprise principally carbon disulfide.

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