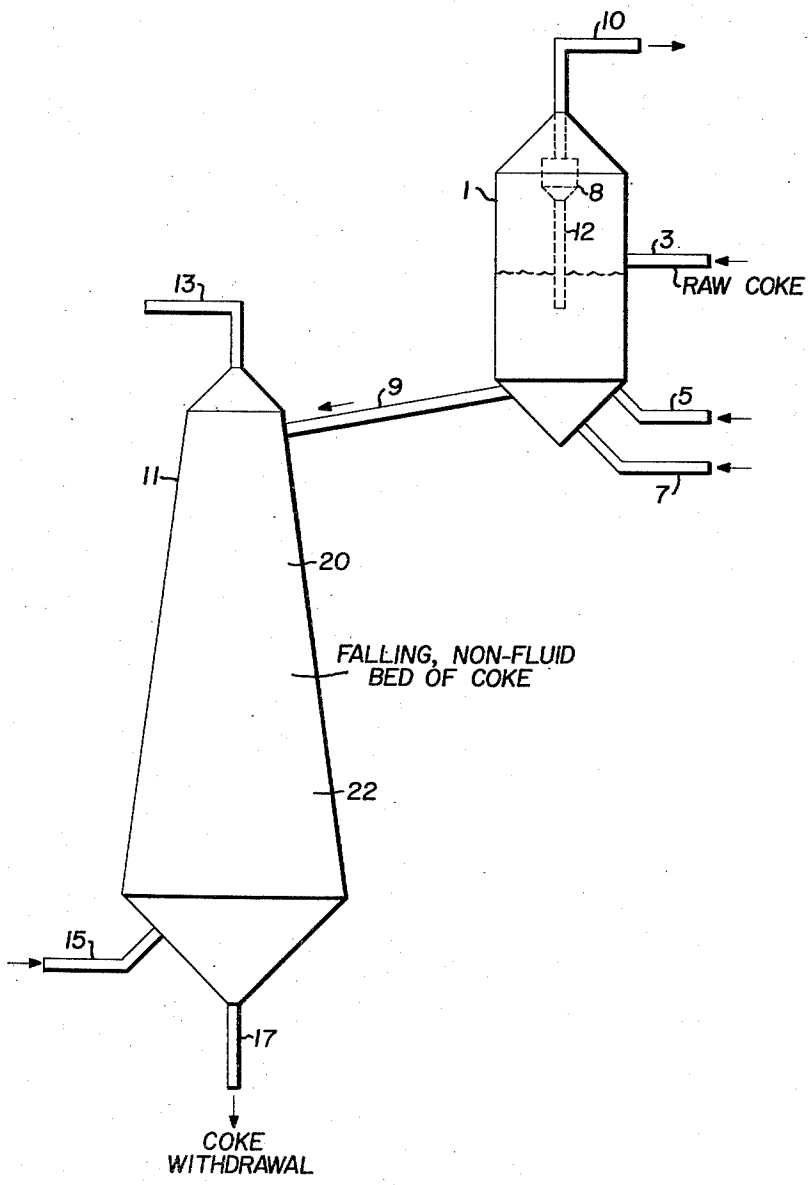
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STAGED CALCINING OF FLUID COKE WITH FALLING, NON-FLUID BED

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STAGED CALCINING OF FLUID COKE WITH FALLING, NON-FLUID BED

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This invention relates to improvements in the desulfurization, devolatilization and increase in electrical conductivity of fluid coke. More particularly it relates to a staged calcining treatment wherein the coke is treated while in the form of a falling, non-fluid bed. The coke is first contacted with a gaseous hydrocarbon at a lower temperature and the evolved hydrogen further treats the coke at a higher temperature.

There has recently been developed an improved process known as the fluid coking process for the production of "fluid coke" and the terminal conversion of heavy hydrocarbon oils to lighter fractions, e. g., see Serial No. 375,088, filed August 10, 1953. For completeness the process is described in further detail below although it should be understood that the fluid coking process itself is no part of this invention.

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 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, 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 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 make 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 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–189–41.)

The method of fluid solids circulation described above is well known in the 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 and lower sulfur and volatile content are particularly necessary before the fluid coke is suitable for manufacture into electrodes, one of the major uses of petroleum coke. The attainment of these properties can be accomplished by calcining the coke at high temperatures, e. g., minimum temperatures of 2100° F. or higher. These temperatures and the times required make the calcining operation relatively difficult and expensive. It is therefore desirable to effect improvements in the calcination and conditioning of the fluid coke.

This invention provides an improved staged calcining operation for achieving this purpose. The process comprises treating the coke in a unitary calcining zone while in the form of a falling, non-flud bed. A normally gaseous hydrocarbon countercurrently contacts the fluid coke in a lower portion of the calcination zone at a temperature in the range of 1800° to 2200° F. The hydrocarbon is cracked to hydrogen and carbon which latter deposits in the voids of the fluid coke. The evolved hydrogen countercurrently contacts the falling fluid coke in an upper portion of the calcination zone at a temperature in the range of 2000° to 2700° F.

The total holdup time in the calcination zone is in the range of about 30 minutes to 6 hours. The temperature in the lower part of the bed is low because of the endothermic heat of the cracking reaction occurring therein. In passing form the bottom to the top of the bed there is first a fairly rapid increase in temperature and thereafter a less rapid increase. The size of the zone of rapid temperature change (which is the zone where most of the cracking is occurring) will depend upon the rate of flow of gas, i. e., for a high rate of flow this zone will be larger than for a low rate of flow. This zone will ordinarily occupy one-tenth to one-half, preferably about one-fourth, of the total bed volume. The time of high temperature treating can thus be in the range of 20 minutes to four hours and the lower temperature in the range of 10 minutes to two hours.

The falling, non-fluid bed is that the same as a moving bed. The particles are substantially not in motion with respect to each other, but the total mass slowly descends through the vessel. The rate of descent is in the range of 1 to 100 ft./hr. depending upon the design of the vessel and upon the contact or residence time desired. The density of the bed is about 55 to 62 lbs./cu. ft.

The velocity of the treating gases, i. e., the evolved hydrogen and the normally gaseous hydrocarbon, is thus kept below that required to fluidize the coke. The linear velocity is the critical one and should be kept below a maximum of about 0.2 ft./sec., preferably about 0.1 ft./sec. or less. This does not depend upon vessel geometry.

The normally gaseous hydrocarbons that can be employed include C_1 to C_4 hydrocarbons such as methane, ethane, propane and butane. Unsaturates such as ethylene, propylene, butylene can also be employed. Methane is particularly preferred and effective. The gas rate as expressed in volumes of gas per volume of coke per hour

(v./v./hr.) will depend upon vessel geometry. For a given linear velocity the v./v./hr. will be higher for a wide shallow bed than for a narrow deep bed. In general the v./v./hr. will be in the range of 20 to 150, preferably about 50 to 75.

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

In heater vessel **1** a fluidized bed of raw coke from line **3** is heated to a temperature in the range of 2000° to 2800° F. e. g. 2700° F. to supply the heat requirements further downstream in the process. A transfer line burner can be used if desired. This heating is accomplished by burning part of the coke with preheated air from line **5**. If desired an alternative fuel such as gas or oil from line **7** may be burned to supply the heat. Flue gases are vented through cyclone **8** and line **10**. Solids are returned to the bed through dipleg **12**.

The heated coke is transferred by line **9** into an upper portion of calcination zone **11**, preferably conical shaped, to provide easy passage of the dense bed. In the upper zone **20** of calciner **11** the falling, non-fluidized fluid coke particles are treated with hydrogen at a temperature in the range of 2000° to 2700° F., e. g. 2600° F. The temperature at the very top of zone **20** will be the same as that of the entering coke, i. e. 2700° F. in the example. However, the temperature in the lower part of this zone will be considerably lower, say about 2200° to 2400° F.

The temperature drop comes about in two ways: (1) heat is needed to heat up the hydrogen from the cracked gases entering below, and (2) heat is consumed in vaporizing the volatile matter of the coke including the sulfur. The hydrogen which has been evolved in a lower zone **22** and which thus countercurrently treats the fluid coke in upper zone **20** is at a linear velocity insufficient to fluidize the coke, less than about 0.2 ft./sec., e. g. 0.1 ft./sec. The hydrogen, hydrogen sulfide, carbon disulfide and other volatiles are removed through line **13**.

The thus desulfurized coke passes into the lower zone **22** of calciner **11**. Here it is countercurrently contacted by preheated methane from line **15**. The methane is also at less than the fluidizing velocity, e. g. 0.05 ft./sec. The amount of methane used is about 40 volumes of methane per volume of coke in zone 22 per hour. The methane is cracked to hydrogen and carbon which deposits in the voids of the fluid coke. The temperature is thus lowered to one in the range of 1800° to 2200° F., e. g. 2100° F. The density and electrical conductivity of the coke is increased. The residence time in the upper zone **20** is 1½ hours and in the lower zone **22** is ½ hour.

The desulfurized coke is withdrawn from a lower portion of the calciner through line **17**.

The particular advantage of hydrogen at elevated temperature in the treatment of "fluid coke" is demonstrated in the following examples.

EXAMPLE 1

In one series of runs the temperature of calcination was varied from 1350° to 2700° F. while using a gas consisting essentially of hydrogen as the treating gas. The coke was treated 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
2,400	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 2000° 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° F. and 2700° F. The coke was treated 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.

Methane gives high coke yields for a given reduction in sulfur content. Although yield values are now 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 carbon of the coke is concerned.

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 of both within the prescribed ranges can bring the sulfur content down to levels required.

The advantages of the process of this invention reside particularly in the fact that in addition to the desulfurization that is obtained, a coke product of high density, purity and good conductivity is provided without requiring an extraneous hydrogen supply.

The sulfur content of the coke can be reduced to be-

low 3 wt. percent and even below 2 wt. percent by the process of this invention and the real density raised to a minimum of 1.8.

The conditions usually encountered in a fluid coker for fuels are also listed below so as to further illustrate how the fluid coke was prepared as distinguished from the treating process of this invention.

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
Coke Circulation (Solids/Oil Ratio)	2–30	7–15

It is to be understood that this invention is not limited to the specific examples which have been offered merely as illustrations and that modification may be made without departing from the spirit of the invention.

What is claimed is:

1. A process for desulfurizing, devolatilizing and increasing the density of fluid coke particles which comprises the steps of feeding heated coke particles to an upper portion of a calcination zone; maintaining the coke particles therein in the form of a falling, non-fluid bed; countercurrently contacting the coke particles under reducing conditions in an upper portion of the calcination zone at a temperature in the range of 2000° to 2700° F. with hydrogen evolved in the lower portion of the calcination zone, the hydrogen velocity being less than

that required to fluidize the coke; countercurrently contacting the thus treated coke in a lower portion of the calcination zone at a temperature in the range of 1800° to 2200° F. with a normally gaseous hydrocarbon at a velocity less than that required to fluidize the coke, the hydrocarbon being cracked to hydrogen and carbon which deposits on the voids of the fluid coke, said cracking cooling the coke to the required temperature and withdrawing calcined fluid coke product from the lower portion of the calcination zone, the total treating time in the calcination zone being in the range of 30 minutes to 6 hours.

2. The process of claim 1 in which the treating time in the upper zone is in the range of 20 minutes to 4 hours, and the treating time in the lower zone is in the range of 10 minutes to 2 hours.

3. The process of claim 1 in which the maximum linear velocity of the hydrogen and the normally gaseous hydrocarbon is 0.2 ft./sec.

4. The process of claim 3 in which the normally gaseous hydrocarbon is utilized in an amount of 20–150 v./v./hr. and the density of the falling, non-fluid bed is in the range of 55–62 lbs./cu. ft.

5. The process of claim 4 in which the normally gaseous hydrocarbon is methane.

References Cited in the file of this patent

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