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COKE CALCINING PROCESS

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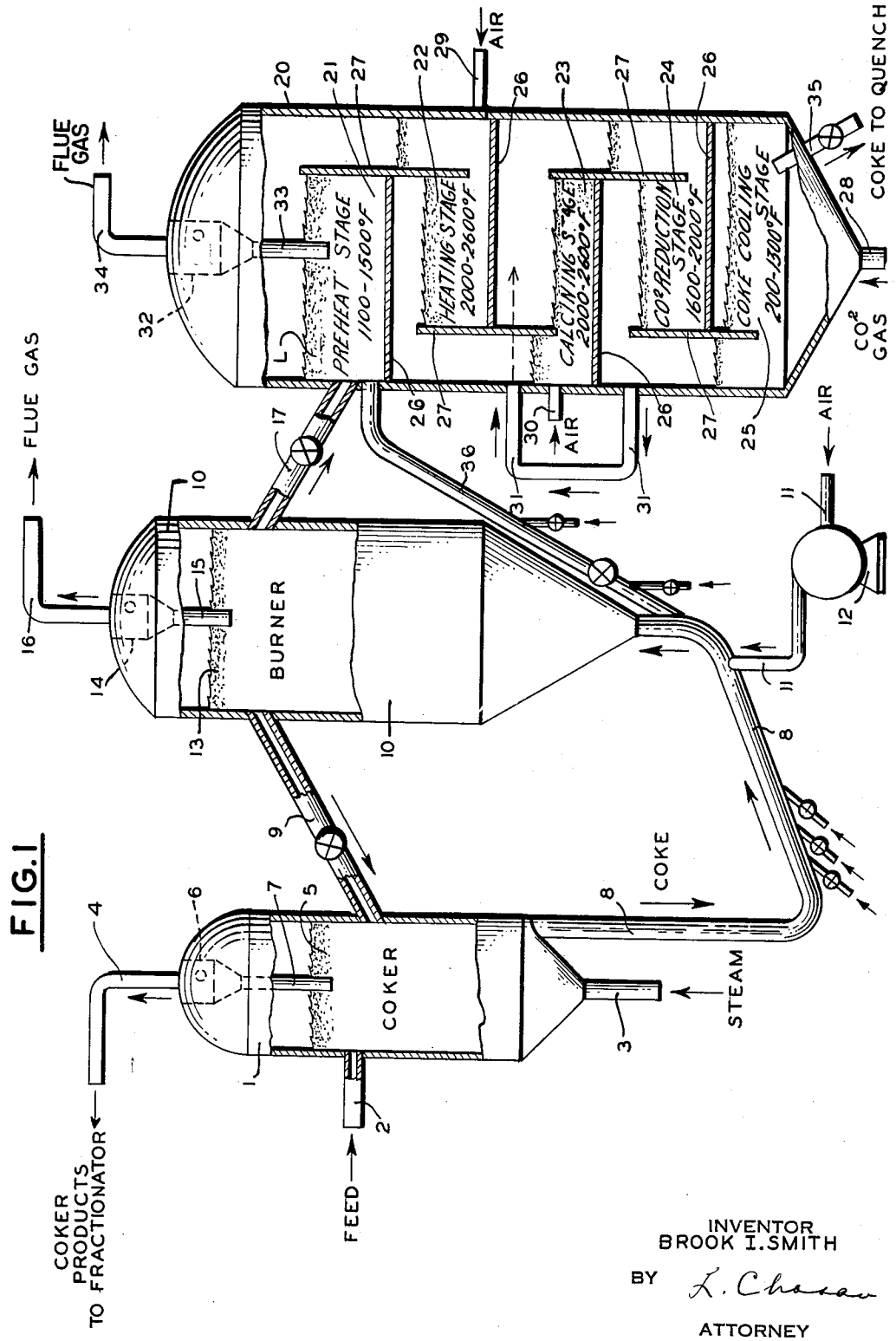


FIG. 1

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COKE CALCINING PROCESS

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This invention relates to a novel coke calcining process.

It is an object of this invention to prepare a coke from petroleum sources which will be useful in the manufacture of carbon electrodes.

It is also an object of this invention to integrate the coke calcining process with the coking process itself.

It is also an object of this invention to provide a multistage process for calcining coke wherein maximum heat economies are effected.

In the coking of heavy hydrocarbon oils such as heavy crudes, crude residua, vacuum still residues, tars, pitches, etc., either for the production of fuel products, such as gasoline and gas oils, or for the production of chemical raw materials, such as aromatics and olefins, one of the major byproducts is petroleum coke. The amount of this material formed depends on the character of the materials being processed and to some extent upon the coking conditions. In the case of high Conradson carbon stock, such as heavy vacuum crude residua, the coke yield may be 20 weight per cent or higher on the residuum. Other stocks have been found wherein the yield may be as high as 35 weight per cent. Since the value of the coke as fuel detracts from a coking process, more attractive uses for the coke have always been sought. One of the major uses to which the coke has been put has been the manufacture of electrodes therefrom. Carbon electrodes find their major use in the electrical refining of alumina to produce aluminum metal. For this purpose petroleum coke is said to be preferable to metallurgical coke which is derived from coal and usually has a high ash content (several per cent) in contrast to petroleum coke in which ash is present only in minor amounts (1% or less). Green (uncalcined) petroleum coke contains volatile matter which must be removed before the material is suitable for electrode purposes. This removal is accomplished by calcining the coke at a high temperature, e. g., 1800° F. or higher, depending on the process employed. The calcining operation reduces the volatile content of the coke to 0.5% or lower of the final product, raises its true density from 1.4–1.5 to 1.80–2.0 or higher, and reduces the electrical resistivity of the coke to 0.015 ohm-inch or lower. Calcining is performed commercially at temperatures of 1800° F. to 2400° F. in rotary kilns, vertical retorts, in electrode baking pits, and other devices. The petroleum coke used today is largely from "delayed" coking plants. In general, and perhaps universally so, the "green" coke is calcined elsewhere than at the site of the coking plant. This is a wasteful practice from the standpoint of unnecessary coke handling and also because of the heat wasted.

There has recently been developed a process known as the fluid coking process. The fluid coking unit consists basically of a reaction vessel or coker and a burner vessel. In a typical operation the heavy oil to be processed is injected into the reaction vessel containing a fluidized bed of inert solid particles, preferably coke particles, maintained at a temperature in the range of 850° F.

to 1200° F., and preferably at 950° F. to 1050° F. for the production of fuels or at a higher temperature, e. g., 1200° F. to 1600° F. for the production of chemicals, i. e., aromatics and olefins. Uniform temperature exists in the coking bed. The uniform mixing in the bed results in virtually isothermic conditions and effects instant 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 thereof.

The heat for carrying out the endothermic coking reaction is generated in the burner vessel. A stream of coke or coke-coated solid inert particles, if the latter are used, 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 on the feed is burned for this purpose. This amounts 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. This coke is preferably withdrawn from the burner for cooling and normally cooled and sent to storage. The coke normally contains about 86% to 94% carbon, 1.5% to 2% hydrogen, 0.5% to 7.5% sulfur, 0.6% to 1.5% volatile matter at 1100° F., up to 6% volatile matter at 950° F., and approximately 0.5% to 3.0% ash at 1100° F.

According to the present invention, coke made in the coking process is transferred continuously without quenching or cooling to a calcining operation. In the calcining operation the coke is subjected to high temperature or high temperature and soaking in order to remove volatile material therefrom, to increase its true density and to lower its electrical resistivity.

In the preferred modification of the invention the coke from the calcining step is cooled by direct contact with a stream of CO_2 or inert gas containing CO_2. The CO_2 reacts with the hot coke to form CO thereby cooling the coke. This CO so produced is burned with air to supply all or part of the calcining heat.

The accompanying figure illustrates one method for integrating the coking and calcining process. Referring to the figure, vessel 1 is a coking vessel constructed of suitable materials for operation at temperatures in the range of 850° F. to 1600° F., e. g. 1000° F. A bed of coke particles preheated to a sufficient temperature, as will be later related to establish the required bed temperature, is made up of suitable particles in the range of 70 to 600 microns. The bed of solid particles reaches an upper level indicated by the numeral 5. The bed is fluidized by means of a gas such as steam entering the vessel at the bottom thereof via pipe 3 at a velocity, e. g. of 2 ft./sec. The fluidizing gas passes upwardly through the vessel establishing the solids at the indicated level. The fluidizing gas serves also to strip the vapors and gases from the coke which flows down into the vessel via pipe 9 as will be later related.

Oil to be converted, e. g. a crude residuum, is preferably preheated to a temperature not above its cracking temperature, e. g. 600° F. It is introduced into the bed of hot coke particles via line 2, 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 4 after passing through cyclone 6 from which solids are returned to the bed via dipleg 7. A stream of solid particles is removed from the coking vessel via line 8 and transported with the assistance of air or other free oxygen-containing gas into burner vessel 10. Air is supplied via line 11 with the assistance of pump 12. In the burner a portion of the carbonaceous materials, e. g. coke or materials deposited thereon, is burned to raise the temperature to a point sufficient to supply the heat to the endothermic reaction occurring in the coking vessel 1. The temperature of the burner solids is usually 150° F. to 300° F. higher than that of the solids in the coking vessel, i. e., about 1000° F. to 1400° F. for fuel production and proportionately higher for production of chemicals and in this example 1200° F. As previously related, about 15% to 30% of the coke made in the process is burned in this vessel. The bed of coke is fluidized in vessel 10 in much the same manner as the bed in vessel 1. The solids are fluidized by the incoming air and resulting combustion gases and are maintained at a level indicated by the numeral 13. Combustion gases leave the hot bed, pass through cyclone 14 and are vented via line 16. Any entrained solids are returned to the bed via dip pipe 15. The hot solids are continually removed from burner 10 via line 9 and introduced into vessel 1 at one or more points in order to maintain heat balance in the system.

The net make coke is removed from the burner via line 17 and introduced into the top stage of a multi-stage treating vessel 20 while CO_2 or inert gas containing CO_2 is introduced into the bottom of the vessel via line 28. Alternatively, coke may be fed directly from the coker to the treating vessel. In this event a portion of the coke being transferred via line 8 from the coker to the burner is diverted to the treating vessel via line 36. The treating vessel 20 consists of a tower containing gas pervious plates and downcomers such as will provide countercurrent contact between downflowing solids and upflowing gases. The vessel contains in descending order, one or more preheat stages 21, one or more heating stages 22, one or more calcining soaking stages 23, one or more reduction stages 24, and one or more cooling stages 25. Uncalcined or green coke enters the top stage which is maintained at a temperature of approximately 1100° F. to 1500° F., preferably 1200° F. to 1400° F. and e. g. 1400° F. This stage serves to preheat the incoming coke by direct contact with hot effluent gases which ascend through the vessel and emerge via uppermost plate 26 to the bottom of bed 21. The effluent gases after passing through the preheating stage enter cyclone 32 for solids removal and are then vented via pipe 34. This gas stream is further cooled, e. g., by passage through a waste heat boiler or by other suitable means for the condensation of volatile material which is removed from the coke in this stage. Any entrained solids are returned via cyclone dipleg 33 to bed 21. In the preheating stage and in each of the subsequent stages in the treating vessel the coke is maintained in the form of a dense turbulent bed on each of the bubble plates 26. The plates permit build up of coke to a level L controlled by the height of the weir of the downcomers 27 which permit passage of coke from one stage to the next lowermost stage. The preheated coke passes to the heating stage 22 wherein it is heated to the required calcining temperature in the range of 2000° F. to 2600° F., preferably 2200° F. to 2400° F., and e. g. 2200° F. The heat required for this stage is supplied by burning in the bed the CO content of the flue gas entering the bed from beneath. For the burning, air is supplied from an external source via pipe 29. The gas residence time in the bed is maintained sufficiently brief, approximately 0.1 to 1 second but may be less than 0.1 second depending upon the temperature required, to selectively burn the CO to CO_2. From the heating stage the hot coke at calcining temperatures is passed to a calcining stage or soaking stage to provide the residence time for calcination. For proper calcination the coke usually requires a residence time of 5 minutes to 8 hours, preferably 30 minutes to 2 hours, e. g. 1 hour, depending upon the temperature employed and the character of the coke undergoing calcining.

Into the calcining soaking stage 23 at e. g. 2400° F. is introduced all of the flue gas from the lower stages, although it may be advisable only to use therein enough gas to fluidize the bed in order to maximize the bed density and to minimize cooling of the bed by the entering cooling gas. It will be observed that the gas below the calcining stage is cooler due to the reduction reaction taking place immediately below. It is sometimes advisable therefore to remove some of the gas from the gas phase beneath the calcining soaking stage 23, allowing it to by-pass the calcining stage, re-introducing the gases to the gas phase directly above the calcining stage. It may sometimes be advisable to perform a small amount of combustion of coke in the soaking or calcining stage in order to maintain sufficiently high calcining temperature therein. This may be done in order to maintain the heating stage at somewhat (say 100° F. or so) lower temperature than the calcining or soaking stage in order to selectively burn the CO to CO_2 without going to extremely short residence time. Should this be the case, combustion is effected by adding a small amount of air via line 30 directly to the calcining bed.

The CO from the CO_2 reduction stage may be withdrawn from the calcining vessel 20 if desired and passed to the burner vessel 10 where it would be burned to CO_2.

From the soaking stage the coke flows to the next lower stage which is referred to as the CO_2 reduction stage 24. In this stage inert gas containing CO_2 is used to burn or react with sufficient coke to convert substantially all (that is, 90–95%) of the CO_2 to CO, thereby providing some or all of the fuel necessary to heat the coke to calcining temperature in the higher stage as previously related or to provide all or a part of the fuel requirements for the coker burner. Reduction of CO_2 to CO is an endothermic reaction, thus it provides heat absorption to cool the coke from the calcining temperature of 2000° F. to 2600° F. to a temperature of 1600° F. to 2000° F., e. g., 1900° F. Further cooling in this stage is accomplished by heat transfer to the cooler entering gas stream. In the reduction stage the gas residence time will be relatively long compared to that required to burn to CO_2 and is of the order of 1 to 10 seconds or longer, e. g., 2 seconds.

From the reduction stage the coke passes to the bottommost stage or cooling stage 25. In this area the coke is further cooled by the gas entering the system via pipe 28 to a temperature in the range of 200°–1300° F., e. g. 1200° F. It is usually advantageous to provide a plurality of stages in this area. Calcined coke product is removed from the lowermost stage via line 35 and is completely cooled by water quenching or other suitable means.

The CO_2 containing gas entering the system via line 28 may be pure CO_2 but is preferably the product of the combustion of natural gas or low cost fuel. In the latter case the combustion products are usually cooled to 100° F. to 150° F. to condense out the water. However, complete removal of water is not necessary.

Although the invention has been described in connection with the integration of the calcining process with the fluid coking process, the calcination may also be applied to the moving bed or fixed bed coking systems. The calcination is not restricted to fluid coke nor to petroleum coke. It is also applicable to coke from high temperature coke desulfurization process or other processes in which coke is available at relatively high temperatures, e. g. Chemico coke from the Chemico sludge

conversion process. However, when employed in conjunction with the fluid coking process the integration offers the following advantages over conventional coking and calcining processes.

1. Uniform calcining temperature which is important to uniform resistivity of electrode coke.

2. Heat economy by using hot fluidized coke directly from the coking unit.

3. Elimination of several steps in conventional calcining processes, i. e., crushing green coke, grinding calcined coke, and screening final product.

4. Completely continuous operation.

5. Simple heating technique.

6. Reduced calcining time; higher temperatures may be used where the temperature is uniform.

What is claimed is:

1. In a process for the calcination of coke the steps of passing finely divided hot coke downwardly through a staged, elongated treating zone, said zone containing in descending order: a preheating zone, a heating zone, a calcining-soaking zone, a reduction zone and a cooling zone and in each zone maintaining the coke in a fluidized state by passing hot coke to be calcined into the preheating zone, simultaneously introducing a CO_2 containing gas into the cooling zone, passing the coke downward through the aforesaid treating zone and the gas upwardly therethrough, heating the coke in the fluidized state in the preheating zone to a temperature of approximately 1100° F. to 1500° F. by means of hot gases emerging from the heating zone, heating the coke in the fluidized state in the heating zone to a temperature in the range of 2000° F. to 2600° F. by means of heat generated in said zone by the combustion with extraneously added air of a gas the carbon content of which consists substantially of CO emerging from the lower calcining soaking zone, maintaining the heated coke in the calcining soaking zone in the fluidized state at a temperature in the range of 2000° F. to 2600° F. for a period of 5 minutes to 8 hours in the presence of a gas the carbon content of which consists substantially of CO, removing the calcined coke from the calcining soaking zone to the reduction zone, contacting the calcined coke in the fluidized state in the reduction zone at a temperature in the range of 1600° F. to 2000° F. with a gas the carbon content of which consists substantially of CO_2 from the cooling zone thereby converting such CO_2 to CO by reaction with the hot coke and effecting cooling of the coke to the 1600° to 2000° F. temperature, removing the coke from the reduction zone to the cooling section where its temperature is further lowered by contact in the fluidized state with incoming cooler gases containing a substantial amount of CO_2 but essentially no CO, removing coke from the cooling zone and removing flue gas from the preheating zone.

2. A process according to claim 1 wherein a small amount of air is introduced into the calcining soaking zone to burn a portion of coke therein and thereby maintain the coke at the calcining temperature.

3. A process according to claim 1 wherein a portion of the gases emerging from the reduction zone bypasses the calcining soaking zone and is introduced into the heating section.

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