July 13, 1965 L. A. WINTER 3,194,753

CONTINUOUS COKING PROCESS AND APPARATUS

Filed Jan. 29, 1963 2 Sheets-Sheet 1

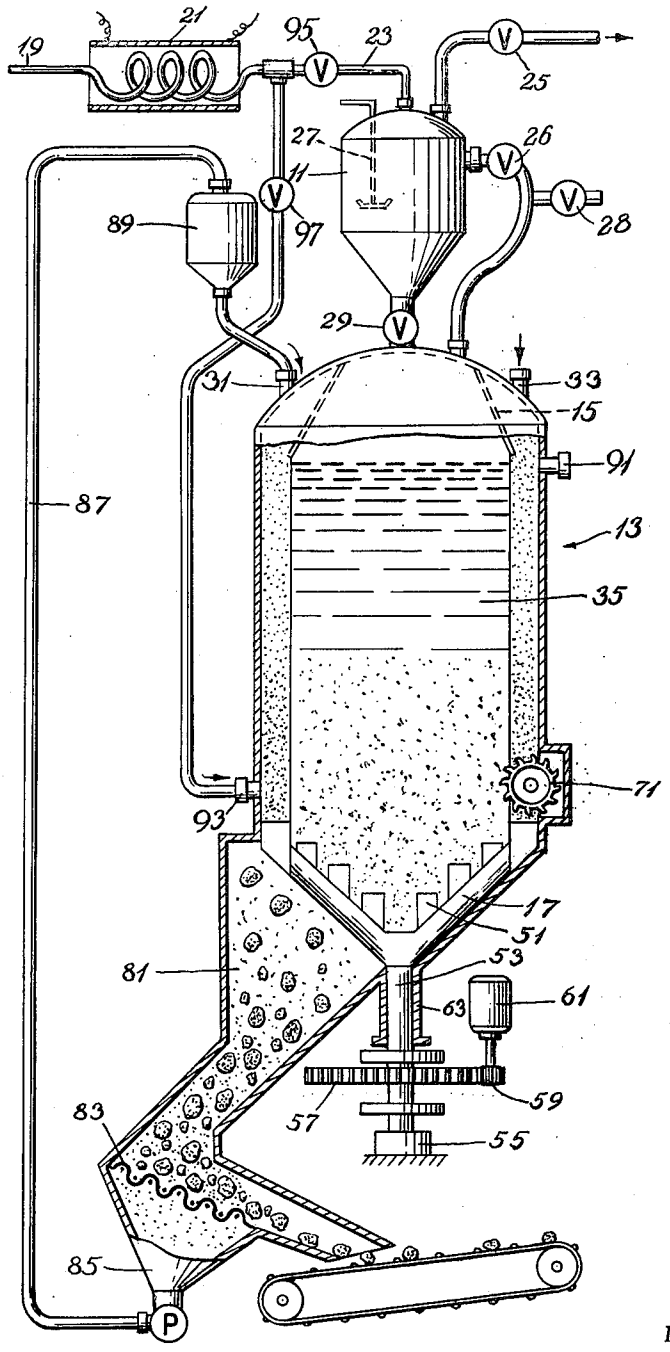


Fig. 1.

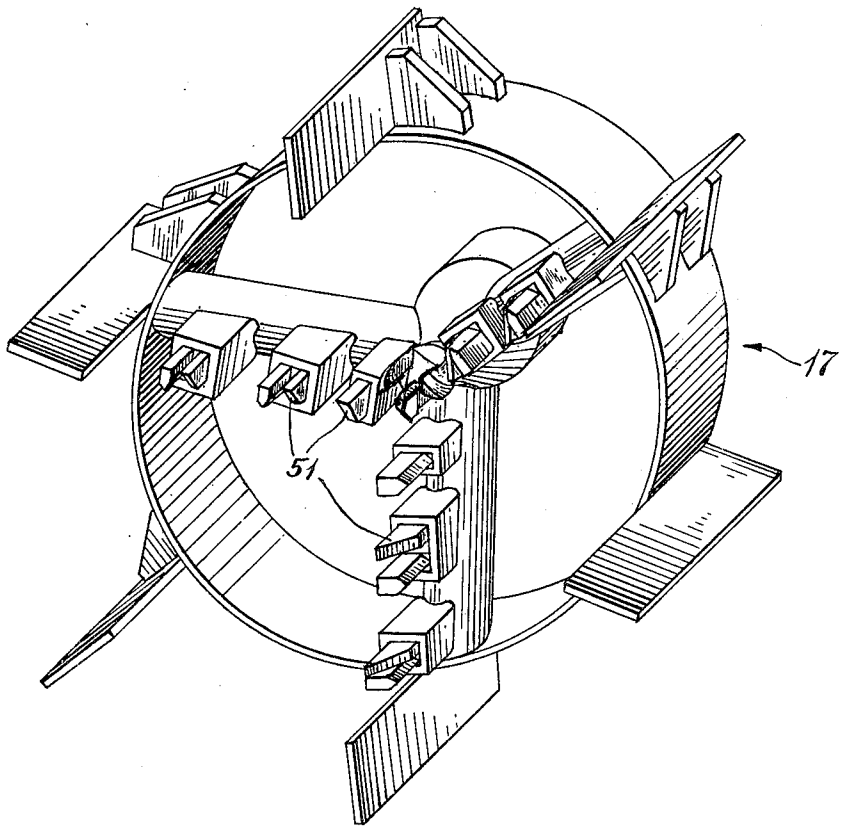
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Filed Jan. 29, 1963 2 Sheets-Sheet 2

Fig. 2.



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CONTINUOUS COKING PROCESS AND APPARATUS

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This invention relates to a method and apparatus for continuously producing coke from thermally polymerizable hydrocarbon fractions, such as pitch, asphalt, and tar.

Nearly all of the high quality, electrode-grade coke produced in the United States is made by a technique termed "delayed coking" in which polymerizable hydrocarbon residues are introduced into coking chambers at high temperatures and are polymerized therein without the benefit of direct heat by merely holding the said residues until coke formation takes place and then periodically cooling and removing the hardened coke. The coking operation normally takes place at about 400° C. to 600° C. at which temperatures the volatile components of the feed material escape and the high-boiling components gradually polymerize, thereby being transformed from a viscous liquid to a hard solid.

The major difficulty inherent in all known delayed coking processes resides in the fact that once the feed material has been fully polymerized into hard coke it adheres to the vessel wall which makes it difficult to remove the coke from the coke drum or other coking vessel. The advances in the art of delayed coking have, therefore, centered around developing procedures for facilitating coke removal and cleaning of the coking vessel.

The labor requirement for cleaning the coke drums was greatly reduced by the advent of "cable pulling" methods for coke removal. Cables were supported in the clean drums by means of wires in a systematic fashion. Upon completion of the coking cycle the bottom closure of the drum was removed and the embedded cables pulled out of the drum with a powered winch. This pulling of the cables resulted in the coke falling out of the drums in chunks and left but a small portion of the drum to be cleaned manually. The cable pulling method was a great advance in the art of delayed coking but installing the cables still required considerable labor and the cables had a limited life so that the industry still desired a better method. The next major advance in the art was the development of hydraulic de-coking methods and equipment. This improvement replaced the "cable pulling" installations rapidly and is today the standard oil industry coking system whenever delayed coking is practiced. In such hydraulic techniques, coke is removed from the drums by means of water jets which cut the body of coke into pieces small enough to drop into a crusher car. A typical assembly is shown and described by Maass et al. in Petroleum Processing, January 1947.

The delayed coking technique is not to be confused with the relatively new fluidized bed and moving bed processes in which coking time is only a few minutes and process heat is supplied continuously whereas, in delayed coking, coking times can approach a full day and the only source of heat is the enthalpy of the feed stream. Coke produced by the various fluidized bed and moving bed processes is generally of fuel value only and not suitable for making electrodes.

As can be seen from the history of the delayed coking are, even the most modern techniques are still batch operations in which equipment must be periodically shut down for coke removal, and thus are subject to the usual disadvantages inherent in discontinuous operation. For example, the coking unit is off stream for substantial periods of time and thus at least two units are necessary for handling a continuous stream of feed material as obtained from an oil refinery. In addition, the equipment used is exposed to alternating periods of high and low temperature and also, during hydraulic coke removal, to contact with water and wet steam and therefore subjected to great strain and corrosion. Also inevitable in the known discontinuous processes is the non-uniform quality of the coke produced as a result of variable coking times for different segments of the polymerizing coke cylinder.

The present invention obviates or mitigates the above-mentioned difficulties and disadvantages by providing a simple, continuous delayed coking process requiring only occasional control by an operator and capable of producing coke of uniform and high, electrode-grade quality.

In essence, my invention comprises providing an annular layer of pulverized coke separating a cylinder of a polymerizing mass comprising polymerizable hydrocarbon fractions from the inside surface of the coking vessel and thereby acting as a sliding surface which prevents adherence of the polymerizing mass to the inside surface of the coking vessel and permits the column of polymerizing mass to progress continuously downward.

The rate of descent of the column of polymerizing mass is conveniently controlled by fragmenting means supporting the said column and fragmenting the fully polymerized coke, preferably by a combined cutting and wedging action.

In a preferred embodiment of this invention the annular layer of pulverized coke proceeds downwardly at about the same rate as the column of polymerizing mass and is recycled to the top of the coking vessel for repeated use, loss of pulverized coke during descent being compensated for by so adjusting said fragmenting means as to provide the necessary amount of pulverized coke to replenish the recycling pulverized coke stream.

A fuller understanding of the present invention and of an apparatus suitable for carrying out a preferred embodiment of the process of my invention can be had by reference to the appended drawing wherein

FIGURE 1 is a vertical cross-section of the overall assembly utilizable in my invention; and

FIGURE 2 is a perspective view of typical fragmenting means forming part of the apparatus of FIGURE 1.

With reference to FIGURE 1, the assembly comprises, as the major components, pre-coking vessel means **11**, substantially cylindrical coking vessel means **13** provided near the top thereof with baffle means **15** comprising a hollow inverted truncated cone disposed in coaxial relationship with said coking vessel means **13**, coke fragmenting means **17** situated at the bottom of said coking vessel means **13**. During steady state continuous practice of my invention, a polymerizable feed stream is continuously introduced through line **19** and heated by heating means such as pipe still heater **21** wherein the feed temperature is raised to the preferred coking temperature. The hot feed stream is then led via line **23** to pre-coking vessel means **11** wherein gases and vapors produced during heating of the feed stream are allowed to escape through escape valve means **25** and wherein some polymerization of the feed materials occurs, the extent of such polymerization being optionally ascertained by viscosity measuring means **27**. Feed material from pre-coking vessel means is controllably introduced through inlet valve means **29** to the upper portion of coking vessel **13**. Simultaneously and continuously introduced in a circumferentially distributive manner through inlet ports such as **31** and **33** is pulverized coke which is then directed to the periphery of the inside surface of coking vessel **13** by baffle means **15** to form an annular layer concentric with said coking vessel **13** and separating a polymerizing mass **35** of feed material from the inside surface of said

coking vessel 13. The annular layer of pulverized coke extends from the top of the bottom of coking vessel 13 to form a hollow cylindrical substantially coaxial with the coking vessel 13 and filled with the polymerizing mass and serving as a sliding surface to permit a gradual descent of the polymerizing mass, the rate of descent being controlled by fragmenting means 17. Fragmenting means 17 can comprise any suitable device known to those skilled in the coke-cutting art capable of achieving a minimum of true cutting and a maximum of wedging action to produce a high percentage of lump coke and a minor amount of pulverized coke. In the embodiment shown, fragmenting means 17 comprises cutter blades 51 extending radially and upwardly from shaft 53 which in turn is supported by thrust bearing 55 and turned by gear means 57 via pinion gear 59 by motor 61. A packing gland 63 provides a seal for the shaft 53 which is also stoutly held in place by bearing 55. The construction of fragmenting means 17 is further illustrated in FIGURE 2 which is a perspective view thereof.

For cases in which shrinkage of the coke cylinders occurs during polymerization, causing the bottom end of said cylinder to be rotated by the fragmenting device, such rotation can be avoided by providing suitable means such as a plurality of circular sharply toothed gears 71 the axes of which are at right angles to the axis of said descending coke cylinder, engaging the coke cylinder circumferentially near the bottom thereof, thereby preventing rotation of the coke cylinder and, in addition, ensuring positive contact of the coke cylinder with fragmenting means 17. The coke lumps and coke fines produced by fragmenting means 17 drop down chute 81 onto screen 83 which directs the coke lumps to a quenching and discharge system well-known to those skilled in the art of coke handling. The coke fines falling through screen 83 are collected in hopper 85 and are advantageously recycled via conveying means 87 and recycle feed bin 89 to coking vessel 13 at points such as 31 and 33. The conveying means 87 can be of any suitable type such as a gas lift, and controllable partial combustion of the coke fines can be provided to maintain the fines at a high temperature, if such is advantageous for forming an effective pulverized coke layer in the coking vessel.

The process as described above is a steady-state continuous one. In the original start-up of the coking unit shown in the preferred embodiment a different procedure is required. The vessel is charged manually with mechanically assists from conventional handling devices well known to those skilled in the art of solids handling. An expendable material such as wood is used to form a temporary barrier facing the fragmenting means 17 to prevent vapors from condensing in equipment below the fragmenting means 17 during the start up operation. Small lumps of coke are then introduced to coking vessel 13 by means of suitable flexible chutes through manholes such as 91. Pulverized coke is introduced through inlet ports 31 and 33 and deposited around the vessel wall by means of a flexible hose while filling the bulk of the vessel with the small lump coke so that a cylindrical column, lined with a pulverized coke layer, is built up. When the bottom of baffle means 15 is reached, additional pulverized coke is added from feed bin 89 through ports 31 and 33 to fill the space between baffle means 15 and the coking vessel walls. The system is tested for gas tightness and the valving set to permit heating of the feed material in coking vessel 13 with hot gas or superheated steam introduced near the bottom of vessel 13 at hot gas inlet 93. The heating means 21 is available for this purpose by closing valve 95 and opening valve 97. The hot gas or superheated steam passes hot gas inlet 93 and upward through the bed of coke lumps out the top of coking vessel 13 and, with valves 29 and 25 open, also brings pre-coking vessel 11 to operating temperature. An expendable tube can be utilized to introduce the heating gases into the middle of the bed of coke lumps without disturbing the pulverized coke layer near the hot gas inlet 93. Once the operating temperature has been reached the hydrocarbon feed stream is temporarily led through the same path as the heating gases, through heating means 21, valve 97 and inlet 93 into the center of the lump coke bed. The feed then percolates upward between the lumps of coke, filling any open spaces and eventually turning to coke. The volatile constituents of the feed continue upward to vessel 11 and bring the entire system to full operating temperature. When the molten polymer reaches the top of the lump coke bed at the lower end of the baffle means 15 the hot hydrocarbon feed stream is switched to the top of pre-coking vessel 11 by opening valve 95 and closing valve 97 and inlet 93. Vessel 11 is allowed to partially fill by closing valve 29 so as to provide some residence time for partial polymerization of the fresh feed while the feed previously introduced to coking vessel 13 is permitted to coke fully by not being diluted with fresh feed. Fragmenting means 17 is then put into operation, valve 29 is actuated by suitable instrumentation to control the flow of partially polymerized heavy residues from vessel 11 so as to maintain the proper level of the reaction mass in vessel 13. The remainder of the equipment operates substantially as set forth above in the description of the continuous process.

Although operating campaigns on this continuous coker would be expected to be quite long, eventual temporary shutdowns for maintenance purposes must be anticipated. A shutdown would be performed by merely causing the flow of feed to cease by closing the proper valves, purging heating means 21 and connected piping, draining the heavy residue from vessel 11 to the top of the coking vessel 13, and continuing coke withdrawal from fragmenting means 17 until the upper level of the heavy residue is lowered to approximately the level of the bottom of the baffle means 15. Operation is thus stopped with the coking vessel full of coke and the fine coke barrier still in place. After such a shutdown, start-up is easily accomplished. The upper portion of vessel 13 is heated by introducing hot gas or super-heated steam through valve 95 into vessel 11; valves 29 and 23 are kept open during this operation while valves 25 and 26 are closed. Hot hydrocarbon feed is then started through heating means 21 with valves 25 and 26 open and valves 29 and 28 closed. As stated in the previous start-up description valve 29 is placed under automatic control after vessel 11 becomes filled to a suitable level, fragmenting means 17 is put into operation, and pulverized coke recirculated continuously.

The term "pulverized coke" as used herein is meant to include coke "fines" or coke "breeze" such as normally obtained in the coke industry as the result of natural breakage in handling and consisting of coke as well as anthracitic fines, coal dust, and the like. Coke fines are preferred in my process because they are essentially nonfusible upon reheating and thus ideal for barrier formation. It will be apparent that other fine inerts, such as sand, clay, or alumina, might serve in place of the pulverized coke, particularly in cases where some contamination of the resulting coke can be tolerated.

The thickness of the pulverized coke layer separating the polymerizing mass from the coking vessel wall, while not narrowly critical, must be sufficient to prevent penetration of said polymerizing mass therethrough in order to aviod adherence of the coke to the vessel wall. The thickness of the pulverized coke layer will therefore depend to some extent on the nature of the feed stream being processed. A feed comprised mainly of heavy residues will be relatively viscous and have little tendency to penetrate through the coke barrier, while a feed comprising lighter hydrocarbon fractions will be less viscous, requiring a thicker coke barrier. When processing coal hydrogenation pitch I have found that coke layer thickness of one inch is sufficient for forming an effective barrier inasmuch as the pitch penetrates only up to one-quarter inch into the barrier.

The temperature of the pulverized coke can be the same as that of the polymerizing mass or it can be higher or lower. Using a relatively cool pulverized coke layer may be advantageous in that the viscosity of the polymerizing mass is extremely temperature-sensitive and increases rapidly upon cooling. Thus, a pulverized coke layer slightly cooler than the polymerizing mass would be even more impervious to penetration thereby. On the other hand, in some applications it may be desirable to introduce the pulverized coke at temperatures above that of the polymerizing mass in order to cause more rapid coking of the polymerizing mass that does penetrate, thereby providing a "skin" for the descending coke cylinder. In such operation it is apparent that the introduction of pulverized coke should be such as to permit substantially identical rates of downward progress for the pulverized coke and the polymerizing cylinder. However, in the general practice of my invention, such identical rates of downward progress are not essential, although preferred. In certain applications it may be desirable to force-feed the pulverized coke at points such as **31** and **33** in FIGURE 1, in order to ensure continuous movement of the barrier annulus. Suitable means of force-feeding would be gas pressure or mechanical means such as a ram or pusher.

It will be understood that the foregoing description has been given with a high degree of particularity so that those skilled in the art may understand fully a preferred embodiment of this invention but that the invention is in no sense limited thereto and variations in apparatus, materials, and operating conditions will be apparent to the skilled artisan.

While the embodiment shown is particularly adapted to processing of pitch-like polymerizable hydrocarbons, my process is applicable to coking of all types of thermally polymerizable hydrocarbon feeds, e.g. coal hydrogenation pitch, coal tar pitch, coal tar, asphalt, crude oil, heavy residuum, and various fractions thereof. If the feed contains low-boiling constituents, vessel **11** could be modified to function as a flash pot and serve to separate the low-boiling materials from the high-boiling compenents of the feed, the latter then being introduced into the main coking vessel.

The following examples are illustrative.

Example I

A hollow steel cylinder with an inside diameter of four inches served as the coking vessel in this experiment. A sheet metal stack having a diameter of three inches was placed inside the said cylinder in coaxial relationship therewith and the resulting cylindrically annular cavity between cylinder and stack was filled with pulverized coke, specifically, metallurgical coke ground so that 99.4 percent by weight passed through an 8-mesh Tyler screen and 17.8 percent by weight passed through a 200-mesh screen. The thus-formed pulverized coke barrier was, therefore, one-half inch thick. A charge of 500 grams of molten coal hydrogenation pitch (viscosity: 64,000 centipoises at 425° C.) was heated to 425° C. and introduced into the cylindrical cavity formed by the said sheet metal stack. The stack was then elevated at the rate of one inch per minute thereby allowing gradual contact of the molten pitch with the said pulverized coke barrier. After the stack was pulled out, the assembly was allowed to remain at 425° C. for six hours. After this time a cylinder of hard coke measuring 3¼ inches in diameter and 4 inches in height and weighing 321 grams was easily removed from the assembly. Examination of the coke cylinder showed that the pitch had penetrated only ⅛ inch into the pulverized coke barrier.

Example II

A hollow steel cylinder with an inside diameter of twelve inches served as the coking vessel in this experiment. A sheet metal stack having a diameter of ten inches was placed inside the said cylinder in coaxial relationship therewith and the resulting cylindrically annular cavity between cylinder and stack was filled with pulverized coke, specifically, metallurgical coke ground so that 93.9 percent by weight passed through an 8-mesh Tyler screen and 9.6 percent by weight passed through a 200-mesh screen. The thus-formed pulverized coke barrier was, therefore, one inch thick. A charge of 40 pounds of molten coal hydrogenation pitch (viscosity 9,600 centipoises at 465° C.) was heated to 465° C. and introduced into the cylindrical cavity formed by the said sheet metal stack. The steel cylinder was then lowered at the rate of one inch per minute with the stack remaining stationary, thereby allowing gradual contact of the molten pitch with the said pulverized coke barrier. After the stack was pulled out, the assembly was allowed to remain at 465° C. for six hours. After this time a cylinder of hard coke weighing 30 pounds was easily removed from the assembly. Examination of the coke cylinder showed that the pitch had penetrated from 1/16 to ¼ inch into the pulverized coke barrier.

Example III

The experiment described in Example II was repeated using molten coal hydrogenation pitch having a viscosity of 20,000 centipoises at 450° C. and heated to 450° C., and, to form the barrier, petroleum coke ground so that 100 percent by weight passed through an 8-mesh Tyler screen and 4.8 percent by weight passed through a 200-mesh screen. The resulting coke cylinder was completely free from the vessel wall and examination showed that the pitch had penetrated only from 1/16 to ⅜ inch into the barrier.

For purposes of comparison, a control experiment was carried out without use of the coke barrier of this invention. A charge of 1600 grams of molten coal hydrogenation pitch was introduced into a steel cylinder six inches in diameter and twelve inches high. A temperature of 460° C. was maintained for three hours. The apparatus was disassembled and the coke was found to be firmly adhering to the cylinder wall. A hammer, chisel, scraper, and wire brush were necessary to clean the coking vessel.

Coke samples produced by known means as well as by the process of this invention were evaluated side-by-side. The results of this evaluation are set forth below.

	1000 C. Coking Value	Apparent Density	Resistance (Ohm-inches)	Thermal Expansion, in./in./° C.
Conventionally prepared coke	94.02	1.483	0.000360	9.8×10^{-7}
Coke from Example I:				
Top	91.40	1.541	0.000357	11.8×10^{-7}
Bottom	90.86	1.541	0.000341	9.7×10^{-7}
Coke from Example II	92.80	1.532	0.000319	10.7×10^{-7}
Coke from Example III	93.00	1.516	0.000337	10.5×10^{-7}

Thus it is noted that coke produced by this invention equivalent in quality to coke produced from the same hydrocarbon feed by standard procedures.

What is claimed is:

1. The method for continuously producing coke from thermally polymerizable hydrocarbon fractions which comprises introducing said hydrocarbon fractions at coking temperatures into a substantially cylindrical vertical coking chamber and maintaining an annular layer of pulverized coke around the inside periphery of said coking chamber so as to separate the polymerizing hydrocarbon fraction from the walls of said coking vessel, and continuously withdrawing hard coke at the bottom of said coking chamber.

2. The method for continuously producing coke from thermally polymerizable hydrocarbon fractions which comprises introducing said hydrocarbon fractions, at coking temperatures, into a substantially cylindrical vertical coking chamber while simultaneously introducing pulverized coke near the top of said coking chamber in circumferentially distributive manner to form an annular layer of pulverized coke around the inside periphery of

said coking chamber so as to separate the polymerizing hydrocarbon fraction from the walls of said coking vessel, and continuously withdrawing hard coke at the bottom of said coking chamber.

3. The method for continuously producing coke from thermally polymerizable hydrocarbon fractions which comprises introducing said hydrocarbon fractions, at coking temperatures, into a substantially cylindrical vertical coking chamber while simultaneously introducing pulverized coke near the top of said coking chamber, in circumferentially distributive manner to form an annular layer of pulverized coke around the inside periphery of said coking chamber so as to separate the polymerizing hydrocarbon fraction from the walls of said coking vessel, continuously withdrawing hard coke at the bottom of said coking chamber, and continuously withdrawing pulverized coke at the bottom of said coking chamber and recycling said pulverized coke to the top of said coking chamber for repeated use.

4. Apparatus for continuously coking thermally polymerizable hydrocarbon fractions comprising substantially cylindrical vertical coking vessel means, baffle means situated near the top thereof capable of circumferentially distributing pulverized coke to form an annular layer of pulveriized coke around the inside periphery of said coking vessel, and coke fragmenting means situated near the bottom of said coking vessel means in operative contact with a descending cylinder of hard coke.

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