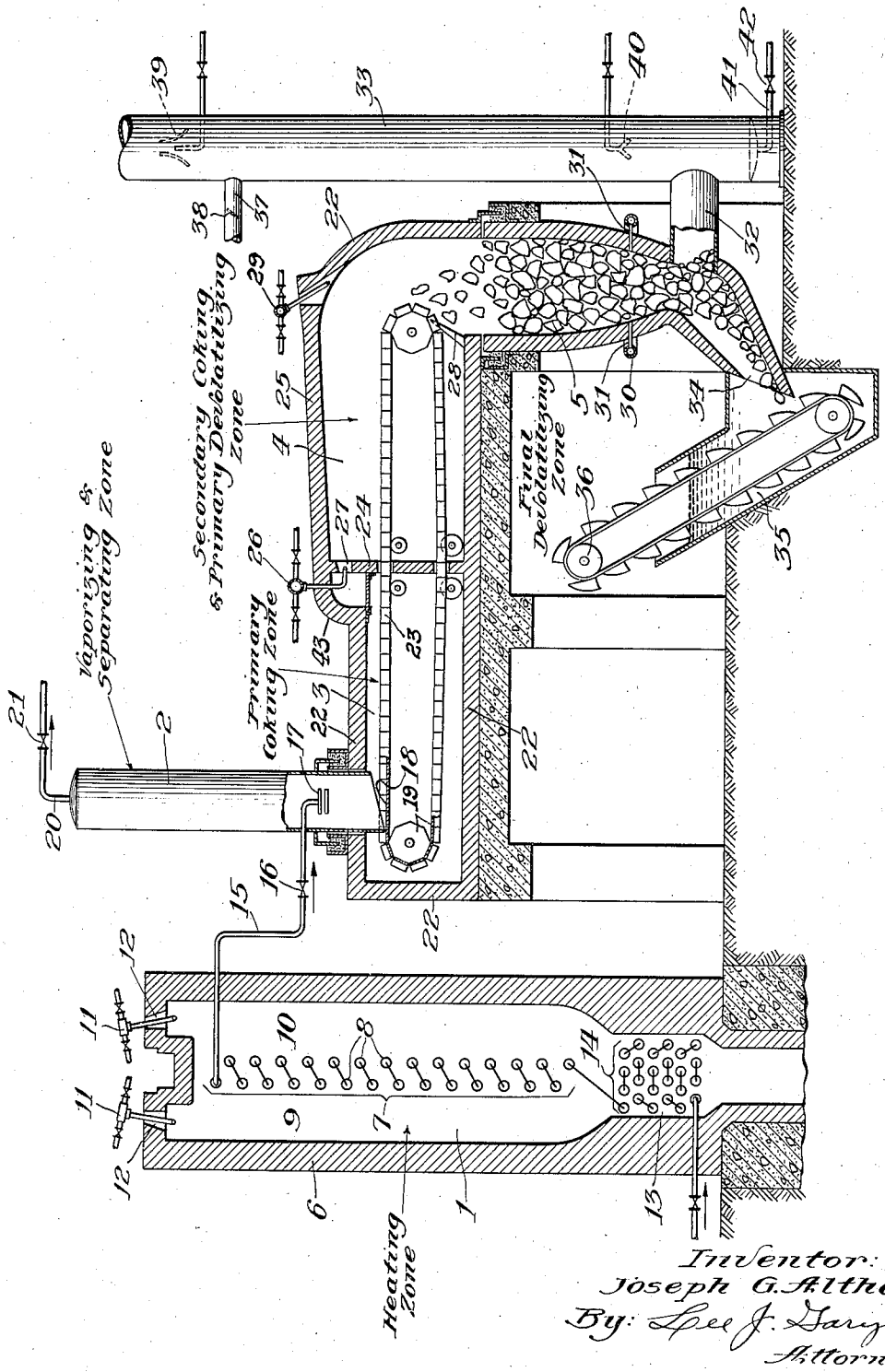
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CONTINUOUS COKING OF HYDROCARBON OILS

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CONTINUOUS COKING OF HYDROCARBON OILS

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This invention particularly refers to an improved process and apparatus for the continuous coking of liquid or semi-liquid hydrocarbons and particularly heavy residual liquids resulting from the pyrolitic conversion of lower boiling hydrocarbon oils.

I have previously disclosed, in my co-pending application Serial No. 745,257 filed September 24, 1934, a process and apparatus for the continuous coking of heavy hydrocarbon oils wherein the heat required for such coking is supplied to the oil by passing the same through a fluid conduit preferably disposed in a special type of furnace designed to employ high rates of heat transfer and quickly heat the oil to a temperature adequate to effect its subsequent reduction to coke without allowing it sufficient time in said fluid conduit to permit any substantial formation and deposition of coke therein. In this previously disclosed process the highly heated products from said fluid conduit are continuously supplied to a coking zone wherein they are reduced to a substantially solid coke-like residue without additional heating, the coking zone preferably employing a continuous conveyor or similar structure whereon the coke-like residue is allowed to accumulate in a relatively thin layer and wherefrom it is continuously removed.

In my co-pending application Serial No. 71,896, filed March 31, 1936, I have disclosed an operation wherein heavy oil to be coked is heated in the manner above described, the heated products separated into vaporous and heavy liquid components or pitch-like residue and the latter supplied to the surface of a continuous conveyor disposed in a coking zone wherein they are reduced to coke by supplying heat directly to the exposed surface of the bed of material accumulated on the conveyor, the resultant coke being continuously removed from the conveyor.

The process of the present invention is similar in many respects to the two processes above outlined, combining advantageous features of each with each other and with additional features, not previously disclosed, in a novel and cooperative manner. This process embodies the steps of quickly heating heavy oil to be coked to a high cracking temperature under non-coking conditions in a fluid conduit, separation of the resultant heated products, preferably at relatively low-pressure, into vaporous components and a heavy pitch-like residual liquid, reduction of the latter to a bed of coke-like residue on the surface of a continuous conveyor, without additional heating, followed by the application of additional heat to the upper or exposed surface of the bed of coke-like material on the conveyor, removal of the coke bed from the conveyor, preferably in the form of relatively small lumps, to expose additional surfaces of the coke mass, further heating of the removed coke to produce a coke of more uniform volatility, and recovery of the resultant products.

I have found that, in continuous coking systems, in general, wherein a bed of coke is allowed to accumulate either upon (1) a heated surface or (2) upon a surface which is not directly heated but whereon the exposed surface of the material undergoing coking is subjected to direct heating, the volatility of the resultant coke and its physical structure will vary considerably from top to bottom of the coke bed, particularly in case the latter is over some two or three inches, at the most, in thickness.

In the improved process of the present invention I am able to produce a coke product of low volatility and of substantially uniform volatility and structure. This is accomplished in a continuous operation and without the excessively strict limitations with respect to the thickness of the coke bed formed on the conveyor necessitated by other continuous coking operations of the same general type but which do not employ the essential steps of the present process in combination.

Particular attention is directed to the fact that all or substantially all of the heat required for the initial reduction of the heavy oil to coke-like residue is contained in the oil entering the coking zone. This feature in itself insures a more uniform grade of coke than could ordinarily be obtained by supplying heat from an external source to the upper or lower surface, or both, of an unpreheated heavy oil. Furthermore, by removing the accumulated bed of coke from the conveyor, preferably in the form of relatively small lumps, new surfaces of the coke are exposed and, by subjecting the mass to further heating, volatiles entrapped in the porous substructure of the coke bed accumulated on the conveyor are released and the coke is thereby more uniformly devolatilized.

Depending upon the specific nature of the oil subjected to treatment in the present process and upon the desired nature of the products it will not be necessary, in all cases, to employ all of the various steps herein provided. The invention also provides for certain alternative methods of treatment which may be selected to suit requirements and are not to be considered equivalent.

One specific embodiment of the invention comprises quickly heating an oil of high coke-form-

ing characteristics to a high cracking temperature at substantial superatmospheric pressure and under non-coking conditions in a heating coil, introducing the highly heated products into a reduced pressure vaporizing zone wherefrom the resultant vaporous products are removed and recovered, supplying the resultant non-vaporous residue, in the form of a heavy pitch-like material, onto the moving surface of a continuous conveyor disposed within a coking zone, causing reduction of said non-vaporous residue to coke-like material without additional heating in the initial stages of the coking operation, subsequently supplying additional heat to the exposed upper surface of the bed of coke-like material accumulated on the conveyor, continuously removing the resultant accumulated coke from the conveyor in the form of lumps and accumulating a substantial mass of the latter, passing hot combustion gases from the coking zone zone through said mass of accumulated coke to reduce its volatile content and recovering the resulting devolatilized coke.

The accompanying diagrammatic drawing illustrates a sectional elevation of one specific form of apparatus embodying the features of the invention.

Referring to the drawing, the apparatus consists essentially of a heating zone 1, a vaporizing and separating zone 2, a primary coking and primary devolatilizing zone 4 and a final devolatilizing zone 5 through which the material undergoing treatment is passed in the sequence given.

The heating zone 1 comprises a furnace structure 6 which, in the particular case here illustrated, is of the type now generally known in the cracking industry as an "equiflux furnace". This type of furnace has a centrally disposed vertical bank 7 of horizontally disposed tubes 8 arranged, in this particular case, in two vertical rows in staggered formation. Tube bank 7 is disposed between and divides the main body of the furnace into combustion and heating zones 9 and 10 to each of which independently regulated amounts of combustible fuel and air are supplied by means of suitable burners 11 through firing ports 12 in the roof of the furnace. The flames and hot combustion gases resulting from the combustion of fuel in zones 9 and 10 are preferably directed at an angle toward the side walls of the furnace structure and passed downwardly thereover to be removed from the lower portion of the furnace through heating zone 13 wherein a separate tube bank 14 may be disposed.

The heavy high coke-forming oil or other hydrocarbon fluid to be reduced to coke is supplied by well known means, such as a pump, not illustrated, from any suitable source to the lower row of tubes in bank 14 and passes in series through the adjacent tubes in each row and through the adjacent rows of tubes in a general upward direction to be transferred from the uppermost row of tubes in bank 14 to the lowermost tube of bank 7. The fluid undergoing heating thence passes in series through adjacent tubes in opposite rows of bank 7 in a general upward direction and is discharged from the uppermost tube of bank 7 through line 15 and valve 16 into vaporizing and separating zone 2.

The fluid passing through tube bank 7 is subjected to high rates of heating primarily by radiant heat supplied directly to the tubes of this bank from the flames and hot combustion gases in zones 9 and 10 of the furnace and from the hot refractory furnace walls. By exposing opposite sides of each tube of this bank to direct radiation in this manner the average rate of heating obtained in this zone may be maintained near the maximum allowable rate, whereby the fluid undergoing treatment is quickly raised to the desired high temperature without allowing it to remain in the heating coil for a sufficient length of time to permit any substantial formation and deposition of coke in this zone. Tube bank 14 is subjected to milder heating conditions, the upper rows of this bank being exposed to radiant heat from the hot refractory walls of the furnace and the hot combustion gases and the entire bank being subjected to heating by direct contact with the hot combustion gases passing from zones 9 and 10 of the furnace to a suitable flue and stack, not illustrated. Tube bank 14 may be eliminated, when desired, but is advantageous as a means of reducing the temperature of the combustion gases leaving the furnace and thereby increasing its thermal efficiency. Other forms of tube bank 7 may, of course, also be employed within the scope of the invention and the possible modifications include a single row of tubes or, when desired, two or more rows of tubes connected either in crisscross arrangement, as illustrated, or in sequence or the various rows of tube bank 7 may, when desired, be connected in parallel.

The invention is, of course, not limited to the use of an equiflux type furnace although this type of furnace is preferred and is distinctly advantageous in combination with the other features of the invention.

The fluid hydrocarbons supplied, as described, to vaporizing and separating zone 2 in highly heated state are separated in this zone into vaporous components and heavy pitch-like residue. To assist this separation I preferably employ a spray arrangement or spreader device, one form of which is indicated at 17, whereby the highly heated fluids discharged from line 15 are directed against the walls of the lower portion of the separating zone, the heavy pitch-like residue flowing downwardly thereover to be discharged from the lower end of this zone onto the upper surface 18 of conveyor belt 19 while the vaporous products pass upwardly through zone 2 to be directed from the upper portion thereof through line 20 and valve 21 to suitable condensing and collecting equipment of any desired form, not illustrated.

Suitable means such as, for example, baffles, perforated pans, bubble trays, packing or the like, or any desired combination of such means, not illustrated, may be employed, when desired, in the upper portion of vaporizing and separating zone 2 for the purpose of assisting removal of entrained or dissolved heavy liquid particles from the vapors prior to condensation of the latter and, when desired, the vaporous products from zone 2 may be subjected to fractionation for the separation of their relatively low-boiling and high-boiling components in a separate fractionating zone, not illustrated, or in an extension of zone 2.

In the particular case here illustrated the primary coking zone 3 and the secondary coking and devolatilizing zone 4 comprise a single structure having insulated refractory walls 22 and containing a suitable continuous conveyor 19 motivated by any well known means, not illustrated, the conveyor preferably being of the type em-

ploying a sectional belt composed of any suitable metal or metallic alloy capable of withstanding the relatively high temperatures to which it is subjected and preferably having flanged edges 23 for retaining thereon a substantial bed of the material undergoing coking. The inlet end of the conveyor is located in primary coking zone 3 and the discharge end in zone 4 and preferably zones 3 and 4 are divided by means of a suitable partition, one form of which is indicated at 24.

The heavy pitch-like residue supplied to the inlet end of conveyor 19 from separating zone 2 is reduced to a bed of coke-like residue on that portion of the conveyor passing through zone 3 without supplying additional heat thereto and the resultant bed of coke-like material then passes on the moving conveyor into zone 4 wherein additional heat is supplied to the upper surface of the bed primarily by radiation from the heated refractory roof 25 of this zone and from the flames of hot gases resulting from combustion therein.

In the particular case here illustrated a suitable burner or air injector 26 is provided through which air or a mixture of combustible fuel and air is supplied to zone 4, and, when desired, the vaporous hydrocarbons evolved from the pitch-like residue undergoing coking in zone 3 may be directed through opening 27 in partition 24 by the injector action of the materials discharged from the device 26 whereby said vapors are admixed with sufficient air to cause their total or partial combustion in zone 4. Preferably the combustible materials supplied to zone 4 are directed at an angle toward the inclined roof 25 of this zone in such a manner that the flames and hot combustion gases will sweep the roof and heat it to a highly radiant condition. Damper 43 is provided for regulating the flow of vaporous products from zone 3 into zone 4 through firing port 27.

In zone 4 the coke, and particularly that adjacent the exposed surface of the bed, is subjected to devolatilization by means of the heat supplied thereto and the resultant coke bed is removed from the discharge end of the conveyor, preferably in the form of lumps which pass from zone 4 into the final devolatilizing zone 5, wherein an appreciable mass of coke is allowed to temporarily accumulate. A suitable scraper or the like such as indicated, for example, at 28 may be provided for the purpose of shearing the accumulated coke from the surface of the conveyor and, when desired, water or steam jets may be directed by well known means, not illustrated, onto the surface of the coke or onto the conveyor belt near the discharge end of the conveyor to assist in breaking the same therefrom.

The coke mass accumulated in zone 5 is subjected to further devolatilization by further heating the same and this final devolatilizing step is rendered particularly efficient by virtue of the fact that the coke mass is in the form of a multiplicity of relatively small lumps and therefore has a much greater exposed surface than the bed of coke on the conveyor. Heating of the coke mass in zone 5 may be accomplished by one or a combination of several methods. One method comprises passing the hot combustion gases from zone 4 downwardly through the mass of coke in zone 5 and, when desired, additional air or additional air and combustible fuel may be admixed with the hot combustion gases prior to their passage through zone 5 by means of one or a plurality of suitable burners or air injectors 29. Such additional air, when used alone, causes further combustion in zone 5 of the partially burned fuel supplied to zone 4 when incomplete combustion is employed in the latter zone. Provision is also made for supplying additional air directly to zone 5 and into the mass of coke accumulated therein at any desired point or plurality of points in this zone by means of header 30 and tuyères 31. When desired, by supplying a sufficient quantity of additional air to zone 5, either through injector 29 or tuyères 31, or both, partial combustion of the coke mass and the volatile hydrocarbons evolved therefrom in this zone may be accomplished. The combustion gases are discharged from the lower portion of zone 5 through flue 32 to a suitable stack 33 and the devolatilized coke passes through a suitable discharge port 34 into a quenching tank 35 wherein a suitable liquid level may be maintained to seal the discharge end of zone 5 and wherein a suitable conveyor 36 may be disposed for removing the quenched coke.

In some cases the combustion gases discharged from zone 5 will comprise a mixture of combustion gases and unburned hydrocarbons resembling producer gas, in which case this material may be recovered for use as fuel within the system or for any other desired purpose by directing the same from stack 33 through flue 37, controlled by damper 38 to a suitable fan or blower, not illustrated, wherefrom it may be supplied to storage or to zones 1, 4 or 5 of the system or elsewhere, as desired. In such cases the fan or blower, not illustrated, may serve as a means of maintaining subatmospheric pressure in preceding portions of the system such as zone 5 or zones 4 and 5. When the gaseous products from zone 5 are not recovered a suitable air inlet device such as illustrated, for example, at 39 may be employed in stack 33 to induce sufficient draft for maintaining subatmospheric pressure in zone 5 or zones 4 and 5.

Preferably heavy tars and pitch-like material are removed from the gaseous products discharged from zone 5 by means of a suitable water spray 40 positioned in the lower portion of stack 33 which serves to scrub out or condense the heavy materials and the latter may be removed from the lower portion of stack 33 through line 41 controlled by valve 42.

In an apparatus such as illustrated and above described the preferred range of operating conditions for accomplishing the desired results may be approximately as follows: The temperature of the fluid hydrocarbons discharged from heating zone 1 may range, for example, from 850 to 1100° F., or thereabouts, and preferably a superatmospheric pressure of the order of 50 to 150 pounds, or more, per square inch is employed in the heating coil. As previously mentioned, the time element in this zone is sufficiently short to obviate any substantial formation and deposition of coke in the heating coil and communicating lines. Any desired pressure ranging from subatmospheric to a superatmospheric pressure no greater than that employed at the outlet from the heating coil may be utilized in the succeeding vaporizing and separating zone and in the primary coking zone and preferably the primary coking zone is operated at a slightly higher pressure than that employed in the secondary coking and primary devolatilizing zone whereby any leakage of gases through partition 24 will be in the direction of the latter zone and the vaporous hydrocarbons evolved in the primary coking zone will not be contaminated by combustion gases, a major portion of said

vaporous hydrocarbons passing from the primary coking zone to the vaporizing and separating zone when damper 43 is closed.

The devolatilizing zones are preferably operated at substantially atmospheric or subatmospheric pressure, although low superatmospheric pressures may be employed therein, when desired. The average temperature of the material undergoing coking in the primary coking zone will, of course, vary depending upon the temperature employed at the outlet from the heating coil and may range, for example, from 800 to 1000° F., or thereabouts. Preferably sufficient additional heat is supplied to the coke bed in the secondary coking and primary devolatilizing zone to maintain the exposed surface of the coke bed near the discharge end of the conveyor at a temperature of the order of 1000 to 1100° F., or more, and the mass of coke accumulated in the final devolatilizing zone is preferably maintained at substantially the same or a higher temperature.

As a specific example of the operation of the process of the invention, a heavy residual oil of high coke-forming characteristics resulting from pyrolytic conversion of lower boiling hydrocarbon oils is supplied from a cracking system to the heating zone of the present process wherein it is quickly heated to an outlet temperature of approximately 1000° F. at a superatmospheric pressure of about 150 pounds per square inch. The heated products are discharged at substantially atmospheric pressure into the lower portion of the vaporizing and separating zone wherefrom their vaporous components are recovered and the non-vaporous pitch-like residue is discharged onto the surface of the conveyor in the primary coking zone at a temperature of approximately 970° F. The conveyor is moved at a sufficiently slow rate to permit the heavy pitch-like residue sufficient time in the coking zone for the evolution of a major portion of its vaporizable components leaving a bed of coke-like residue on the conveyor. A major portion of the vapors evolved in the primary coking zone are directed therefrom to the vaporizing and separating zone but a small portion of these materials pass through the ports in the partition dividing the primary coking zone from the secondary coking and primary devolatilizing zone, in which latter zone they serve as fuel. The vaporizing and separating zone and the primary coking zone are operated at substantially atmospheric pressure and a slight subatmospheric pressure is employed in the succeeding portions of the system. The bed of coke on the conveyor leaves the primary coking zone at a temperature of approximately 920° F. and the exposed surface of the bed is heated in the secondary coking and primary devolatilizing zone to a temperature of approximately 1100° F. by the partial combustion of fuel adjacent the roof of this zone. The partially burned gases from the secondary coking and primary devolatilizing zone enter the mass of coke accumulated in the final devolatilizing zone admixed with a small amount of additional fuel and sufficient additional air to cause substantially complete combustion of the mixture in the latter zone. The burning gases pass downwardly through the mass of coke which they serve to heat and the resultant devolatilized coke is quenched and discharged from the system.

The above operation will yield, per barrel of residual oil charged to the system, approximately 150 pounds of coke having a volatility of less than 4 per cent by weight and a substantially uniform quality. In addition about 25 per cent by volume of the charging stock is recovered as liquid hydrocarbons, the remainder being chargeable to uncondensed gases and loss.

I claim as my invention:

1. A process for the continuous coking of hydrocarbon oil, which comprises heating the oil at substantial superatmospheric pressure and under non-coking conditions to a temperature adequate to effect its subsequent reduction to coke-like residue, separating vaporizable components of the resultant heated products from the non-vaporous fluid residue, discharging the latter onto the moving surface of a continuous conveyor, causing the further evolution of vapors and reduction of fluid residue to coke-like residue, in the form of a bed on said surface of the conveyor, without additional heating, subsequently passing the bed of coke-like material on said surface of the conveyor through a zone in the coking stage wherein it is subjected to additional heating and further devolatilized by heat supplied directly to the exposed surface of said coke bed, removing the resultant coke from the conveyor in the form of lumps following the last mentioned stage of treatment, passing hot combustion gases over the newly exposed surfaces of the coke to further devolatilize the same, and recovering the resultant products.

2. A process for the continuous coking of hydrocarbon oil, which comprises heating the oil at substantial superatmospheric pressure and under non-coking conditions to a temperature adequate to effect its subsequent reduction to coke-like residue, separating vaporizable components of the resultant heated products from the non-vaporous fluid residue, discharging the latter onto the moving surface of a continuous conveyor, causing the further evolution of vapors and reduction of fluid residue to coke-like residue, in the form of a bed on said surface of the conveyor, without additional heating, subsequently passing the bed of coke-like material on said surface of the conveyor through a zone in the coking stage wherein it is subjected to additional heating and further devolatilized by heat supplied directly to the exposed surface of said coke bed, breaking the coke bed into a multiplicity of pieces whereby to expose the additional surfaces of the coke, continuing heating of the newly exposed surfaces of the coke to effect further devolatilization thereof, and recovering the resultant products.

3. A process for the continuous coking of hydrocarbon oil, which comprises heating the oil at substantial superatmospheric pressure and under non-coking conditions to a temperature adequate to effect its subsequent reduction to coke-like residue, separating vaporizable components of the resultant heated products from the non-vaporous fluid residue, discharging the latter onto the moving surface of a continuous conveyor, causing the further evolution of vapors and reduction of the fluid residue to coke-like residue, in the form of a bed on said surface of the conveyor, without additional heating, subsequently passing the bed of coke-like material on said surface of the conveyor through a zone in the coking stage wherein it is subjected to additional heating and further devolatilized by heat supplied directly to the exposed surface of the coke bed, breaking the coke bed into a multiplicity of pieces whereby to expose the additional surfaces of the coke, accumulating a mass of the broken coke, passing hot combustion gases through said

mass in contact with the newly exposed surfaces of the coke pieces whereby to additionally devolatilize the coke mass, and recovering the resultant products.

4. A process such as defined in claim 3 wherein said combustion gases passing through said accumulated mass of coke are derived, at least in part, from the combustion of fuel in the previously mentioned zone of the coking stage.

5. A process such as defined in claim 3 wherein the hot combustion gases passed through said accumulated mass of coke are derived, in part, from the combustion of fuel in the previously mentioned zone of the coking stage and, in part, by the addition of fresh increments of hotter combustion gases.

6. A process such as defined in claim 3 wherein heat supplied to said exposed surface of the bed of coke on the conveyor is derived by the incomplete combustion of hydrocarbons in that zone of the coking stage wherein the heating of said surface is effected and wherein incompletely burned products of said combustion are mixed with additional air and passed through said coke mass to effect their further combustion and further heating of the coke mass.

7. A process such as defined in claim 3 wherein at least a portion of the heat supplied to said exposed surface of the coke bed on the conveyor is derived from the combustion of volatile hydrocarbons evolved in the same zone of the coking stage.

8. A process such as defined in claim 3 wherein at least a portion of the heat supplied to said exposed surface of the coke bed on the conveyor is derived from the combustion of volatile hydrocarbons evolved from the material undergoing coking in the preceding stage of the operation.

9. An apparatus for the continuous coking of fluid hydrocarbons, which comprises, in combination, a coking and devolatilizing oven, said oven being divided into a primary coking zone, a secondary coking and primary devolatilizing zone and a final devolatilizing zone, a continuous conveyor disposed within the two first mentioned zones, means for supplying the fluid hydrocarbon to be coked onto the surface of said conveyor in the primary coking zone in highly heated state, whereby to accumulate a bed of coke-like residue on said surface, means for removing from the primary coking zone vaporous products evolved from the fluid hydrocarbons undergoing coking therein, means for supplying additional heat to the exposed surface of said bed of coke-like residue on the conveyor in the secondary coking and primary devolatilizing zone, means for removing the resultant coke from the conveyor in the latter zone, means for supplying the removed coke to the final devolatilizing zone and accumulating a substantial mass of the same therein, means for passing hot combustion gases from the secondary coking and primary devolatilizing zone through said mass of coke in the final devolatilizing zone and means for recovering the devolatilized coke from the latter zone.

10. An apparatus for the continuous coking of fluid hydrocarbons comprising, in combination, a primary coking chamber, a secondary coking and primary devolatilizing chamber and a final devolatilizing chamber, means for supplying the fluid hydrocarbon to be coked into the primary coking chamber in highly heated state and accumulating a bed of coke-like residue therein, means for transferring said bed of coke-like residue into the secondary coking and primary devolatilizing chamber, means for heating the exposed surface of the coke bed in the latter chamber, means for transferring the coke from the secondary coking and devolatilizing chamber to the final devolatilizing chamber, means for accumulating a substantial mass of said coke in the latter zone, means for supplying additional heat to said coke mass and means for removing the devolatilized coke from the final devolatilizing zone.

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