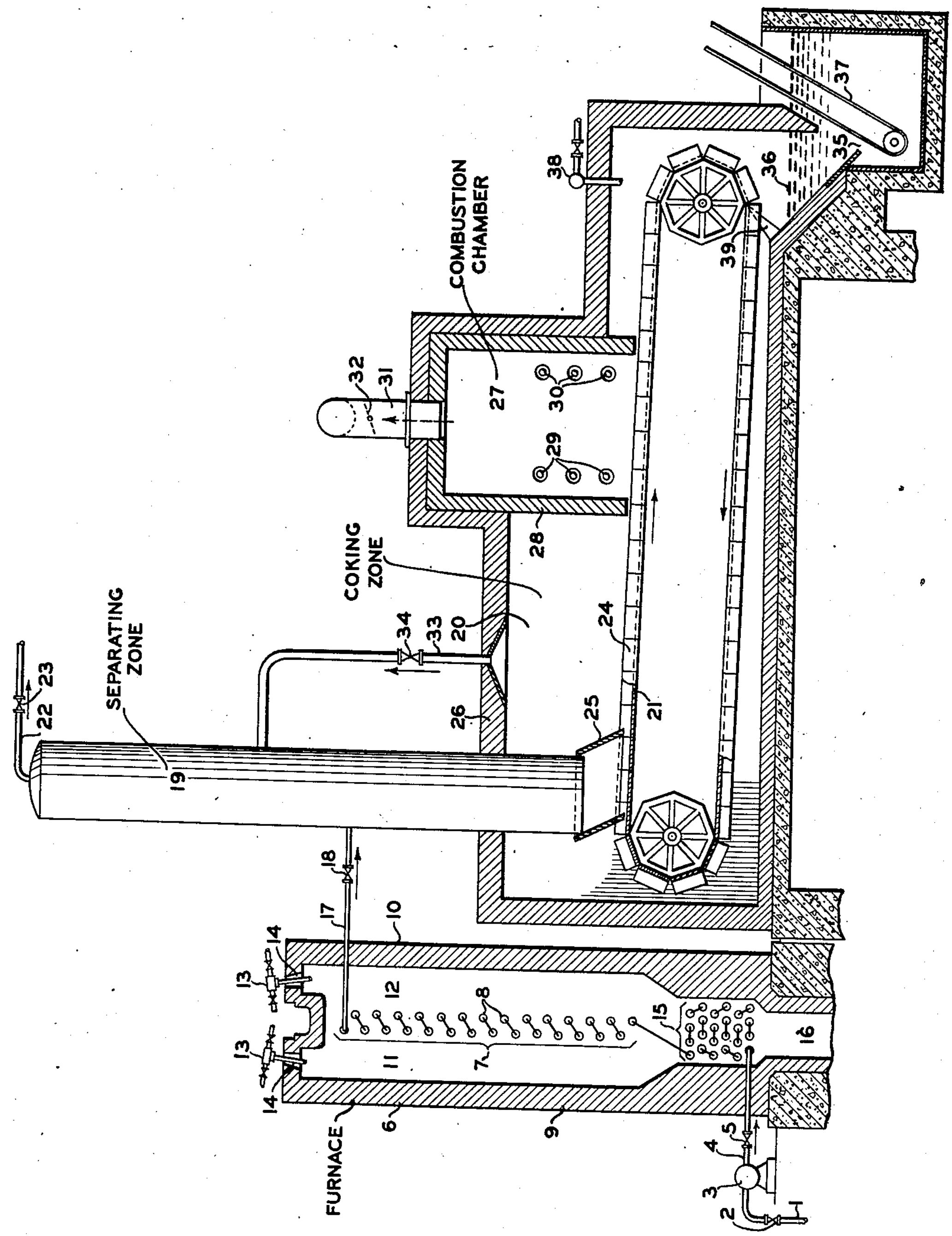
Nov. 7, 1939. J. G. ALTHER 2,179,080

COKING OF HYDROCARBON OILS

Original Filed March 31, 1936



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Patented Nov. 7, 1939

2,179,080

UNITED STATES PATENT OFFICE

2,179,080

COKING OF HYDROCARBON OILS

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Continuation of application Serial No. 71,898, March 31, 1936. This application February 20, 1939, Serial No. 257,288

2 Claims. (Cl. 196—69)

This is a continuation of my application, Serial No. 71,898 filed March 31, 1936, which has now become abandoned.

This invention particularly refers to an improved process and apparatus for the pyrolytic conversion of heavy hydrocarbon oils, such as residual oils, particularly those resulting from the cracking of lower boiling oils and also including mixtures of hydrocarbon oil and solid or semi-solid pyro bituminous materials, such as coal, accompanied by continuous coking of the resulting tar-like residue on a continuous conveyor by means of heat applied directly to the upper surface of a relatively thin bed of said heavy pitch-like residue on the conveyor.

Many operations have previously been proposed for the continuous coking of heavy residual oils. Some of these employ externally heated rotary retorts or continuous conveyors of vaporous types wherein the heat for coking is passed through metal or refractory material upon which the coke is deposited. Obviously, this necessitates excessive heating of the metal or refractory surface upon which the coke is deposited in order to supply sufficient heat through the bed of material undergoing coking to effectively coke its upper portions and, even when the material to be coked is confined to a relatively thin layer the useful life of the heated surface upon which the coke is deposited is relatively short and the characteristics of the coke produced vary considerable, particularly with respect to volatility and hardness, due to excessive heating of the lower portions of the layer and insufficient heating of the upper portions. Other operations which have been proposed apply heat directly to the upper surface of the materials undergoing coking by combustion in the vapor space above the coke bed which, of course, involves at least partial combustion of the volatile hydrocarbons evolved from the materials undergoing coking. Each of these two types of operations possess certain advantages. By employing the first mentioned process contamination of the volatiles evolved from the materials undergoing coking with combustion gases and/or actual combustion of the hydrocarbons evolved may be prevented while, by employing the second mentioned process, excessive heating of the surface upon which the coke accumulates may be avoided. The present invention retains the advantages of both of the previously proposed processes above mentioned and obviates the disadvantages of each.

Another method of continuous coking which is now used extensively provides for introducing the relatively heavy oil to be coked in highly heated state into alternately operated coking zones wherein coking is accomplished either by the excess heat contained in the heavy oil supplied to the coking zone or by introducing a suitable heat carrying medium into the body of material undergoing coking. This is probably the most satisfactory method which has been employed for coking heavy residual oils such as those resulting from cracking but involves the rather cumbersome and inefficient procedure of switching and preconditioning the coking zones. The present invention also retains the advantages of this method, which eliminates the disadvantages of both of the other methods previously described, and in addition obviates the use of alternately operated coking zones.

In the preferred embodiment of the invention, the relatively heavy oil to be coked is passed through the heating coil of a furnace, which is preferably of the general type previously disclosed by me, wherein it is quickly heated, under non-coking conditions, to a sufficiently high temperature to effect subsequent substantial coking thereof. The highly heated oil is then passed into a separating zone preferably operated at substantially atmospheric or relatively low superatmospheric pressure wherein its vaporous components are separated from the resulting nonvaporous liquid residue, the vaporous products are removed from the separating zone and may be subjected to condensation for the recovery of their condensable components and separation of the same from uncondensed gases or they may first be subjected to fractionation for the separate recovery of one or more selected intermediate or high-boiling fractions. The liquid residue, which is separately removed from the separating zone at high temperature in the form of a relatively heavy pitch-like residue, is continuously discharged onto the upper surface of a continuous belt-type conveyor disposed within a suitable furnace structure. The pitch-like residue is caused to spread out in a relatively thin body of extended surface over the upper surface of the moving conveyor-belt and is reduced thereon to a relatively thin mass of coke-like material partially by its contained heat and partially by heat radiated thereto by the relatively hot refractory walls of the combustion chamber of the coking zone. The coke-like mass then continues on the conveyor beneath the combustion chamber of the coking furnace which may be relatively small in relation to the whole furnace structure and is separated from the remaining portion thereof by refractory walls, preferably of high heat conductivity, which radiate heat to the materials undergoing coking in the preceding zone of the coking furnace. Combustible materials are introduced directly into the combustion chamber and heat is supplied from the resulting hot combustion gases and the hot refractory walls of this zone directly to the upper surface of said relatively thin coke-like mass upon the conveyor whereby its reduction to relatively dry coke is completed after a substantial amount of volatiles have been evolved therefrom in the preceding zone of the coking furnace, out of contact with the combustion gases. Combustion products are removed from the combustion zone without allowing any substantial quantity thereof to commingle with the volatiles evolved in the preceding coking stage, the latter being returned to the separating zone wherefrom they are removed to subsequent treatment with the other vaporous products from this zone and the coke is subsequently removed from the conveyor and discharged from the system, preferably after quenching.

The advantages which accrue from the various features of the invention will be apparent to those familiar with ordinary cracking and coking operations from the above description and from the accompanying diagrammatic drawing and following description thereof. The drawing is a view in side elevation, with parts in section, of one specific form of apparatus in which the operation of the process may be accomplished.

Referring to the drawing, the heavy oil charging stock, which may comprise, for example, liquid residue from a cracking operation or from storage or any other heavy fluid or semi-fluid hydrocarbon from any desired source, is supplied through line 1 and valve 2 to pump 3 by means of which it is fed through line 4 and valve 5 to the heating coil of the system which is located within furnace 6.

Any desired type of furnace may be employed which is capable of quickly heating the heavy oil to a sufficiently high temperature to effect its subsequent reduction to heavy pitch or coke-like residue, without allowing it to remain in the heating coil for a sufficient length of time to permit substantial coke formation and deposition therein. The furnace here illustrated is of the general type previously disclosed by me which is now generally known in the industry as an "equiflux" heater. This term is derived from the fact that the main portion of the heating coil or fluid conduit indicated in the drawing at 7 is comprised of a plurality of tubes which are each subjected to substantially equal rates of heating on opposite sides. Tube bank 7, in the case here illustrated, comprises two vertical rows of horizontally disposed tubes 8 arranged in staggered formation so that the opposite sides of each tube are exposed to radiant heat transmitted thereto from the hot refractory side walls 9 and 10 of the furnace and the materials undergoing combustion in combustion zones 11 and 12 located, respectively, between tube bank 7 and walls 9 and 10. Regulated amounts of fuel and air are supplied to each of the combustion zones by means of burners 13 communicating with each of the combustion zones through firing ports 14 in the roof of the furnace, through which firing ports controlled amounts of auxiliary air and/or recirculated combustion gases may be introduced. In the particular case here illustrated, adjacent tubes in opposite rows of bank 7 are connected at their ends in series by means of suitable return bends, as indicated in the drawing by the single lines connecting adjacent tubes in opposite rows, and preferably substantially equal heating conditions are maintained in combustion zones 11 and 12 although, when desired, adjacent tubes in each row of bank 7 may be connected in series and different firing conditions may be maintained in combustion zones 11 and 12. Preferably the burners 13 are pointed at an angle toward the side walls 9 and 10 so that the flames and hot combustion gases impinge upon and wash the refractory walls, heating the same to a highly radiant condition. Since one of the purposes of a furnace of this type is to provide exceptionally high rates of heat transfer to the oil passing through tube bank 7 by employing predominantly radiant heat from the walls and hot combustion gases on opposite sides of each tube, the combustion gases leave zones 11 and 12 at a relatively high temperature and, preferably, in order to increase the furnace efficiency by recovering additional heat from the gases, a separate tank of tubes, indicated in the drawing at 15, is provided beneath combustion zones 11 and 12 and between these zones and flue 16. In this manner heat is imparted to the tubes of bank 15 both by radiation and convection from the combustion gases passing from zones 11 and 12 to flue 16. Flue 16 communicates with a suitable stack, not illustrated, and a suitable damper, not illustrated, may be provided either in the stack or the flue. In the case here illustrated, the heavy oil to be treated flows in a general upward direction through tube bank 15 countercurrent to the general direction of flow of the combustion gases and thence passes through tube bank 7, in the manner already described, to be discharged at a relatively high conversion temperature from the uppermost tube of this bank through line 17 and valve 18 into the separating zone 19.

The heavy residual tar-like products separate from the vaporous components of the products supplied to separating zone 19 and are directed rapidly downward through the lower portion of the separating zone to the coking zone 20 wherein they pass onto the moving surface of conveyor 21 to be reduced thereon to a relatively thin bed of coke. The vaporous products which separate from the relatively heavy pitch-like residue in zone 19 are removed from the upper portion thereof through line 22 and valve 23 and may be either subjected to condensation and the resulting distillate and gas collected and separated or they may be first subjected to fractionation for the separate recovery of any desired intermediate or high-boiling fractions. This portion of the apparatus may be of any well known form and for the sake of simplicity is not illustrated in the drawing.

Conveyor 21, which is motivated by any suitable means, not illustrated, may be any desired type or form of conveyor capable of retaining the pitch-like residue from zone 19 upon its upper surface in a relatively thin body. The conveyor, in the case here illustrated, is a continuous belt-type employing a belt of suitable metal or metallic alloy capable of withstanding the conditions to which it is subjected and having upturned or flanged edges 24 to retain the pitch-like residue on the conveyor before it is coked. Preferably in order to minimize coke deposition in zone 19 there is no substantial restriction in the path of flow of the heavy pitch-like residue from this zone to the surface of the conveyor and in the case here illustrated a spreading device 25 is employed the forward side of which extends to or slightly below the flanged portion 24 of the conveyor belt and assists in spreading out the heavy pitch-like residue in a continuous relatively thin body upon the upper surface of the conveyor. The opposite side of spreader device 25 extends close to the surface of belt 21 in order to prevent the heavy pitch-like residue from flowing over the end of the conveyor. Any other suitable spreading or distributing device may, of course, be employed within the scope of the invention.

Conveyor 21 is disposed within a suitable insulated housing or furnace setting 26 and a portion of the coking zone, which is indicated in the drawing as combustion chamber 27 is separated from the remaining portion by means of suitable walls 28, preferably constructed of refractory material of high heat conductivity such as, for example, silicon carbide. Walls 28 extend horizontally between the side walls of the furnace setting 26 and extend vertically from the roof of the furnace or from a point above the main portion of the roof to near the surface of the coke-like material on the conveyor. In this manner combustion zone 27 is effectively separated from the rest of the coking zone and gases resulting from the combustion fuel in this zone are thereby prevented from commingling with and contaminating the hydrocarbon vapors evolved from the materials undergoing coking in other portions of the coking zone. Suitable burners, the tips of which are indicated in the drawing at 29, communicate with combustion zone 27 through firing ports 30 whereby combustible fuel and air is supplied to this zone and, when desired, the burners may be pointed at an angle toward the refractory walls 28 in order that the hot combustion gases may impinge upon and wash the walls, heating the same to a high temperature. Heat is radiated from the materials undergoing combustion in chamber 27 and from the interior surface of the refractory walls of this zone to the bed of coke-like material on conveyor-belt 21 as it passes immediately beneath the combustion zone. Combustion gases are removed from the upper portion of combustion zone 27 through flue 31 controlled by damper 32 to a suitable stack, not illustrated, and preferably pass on their way to the stack through an economizer section, not illustrated, which may serve, for example, as a means of preheating air for either or both combustion zone 27 and furnace 6. Preferably the draft through flue 31 is so controlled that there is a slight flow of hydrocarbon vapors and gases into combustion zone 27 from the other portions of the coking zone rather than a flow of combustion gases from zone 27 into the other portions of the coking zone.

Preferably combustion chamber 27 is located a substantial distance along the path of travel of the materials undergoing coking on conveyor 21 from the inlet end of the conveyor so that when the material on the conveyor reaches zone 27 it will have been substantially reduced to coke and a major portion of the volatiles will have been evolved therefrom in the preceding portion of the coking zone. In this manner the heat supplied to the coke-like material on conveyor 21 passing beneath combustion chamber 27 will serve to reduce the volatility of the coke to the desired degree after a major portion of the vaporizable hydrocarbons have been liberated from the heavy pitch-like residue from zone 19. As previously mentioned, walls 28 preferably comprise a material of high heat conductivity so that heat will be transmitted through these walls to the materials on the conveyor in other portions of the coking zone to assist vaporization of a major portion of the volatiles from the pitch-like residue before it reaches the combustion chamber.

Hydrocarbon vapors and gases evolved from the pitch-like residue in portions of the coking zone other than combustion zone 27, which are substantially free of contamination with combustion gases generated in combustion chamber 27, are removed from the upper portion of the coking zone and may be directed through line 33 and valve 34 into separating zone 19 wherein they commingle with the hydrocarbon vapors and gases previously separated from the pitch-like residue in this zone or they may be separately supplied to suitable condensing or fractionating equipment, not shown. When desired, suitable means, such as baffles, bubble trays, or the like, may be provided in the upper portion of separating zone 19 to assist in removing any entrained or dissolved heavy pitch-like or other high coke-forming materials from the hydrocarbon vapors and gases, prior to their removal from this zone.

The layer of coke on the conveyor, after passing beneath combustion chamber 27, passes to the discharge end of the conveyor from which it is removed through a suitable discharge port 35, which may be sealed either by mechanical means, not illustrated, or by maintaining a suitable liquid level in the discharge port, such as indicated at 36. In the particular case here illustrated, a suitable conveyor 37 is provided beneath discharge port 35 to remove the coke to cars, not illustrated, or to storage or elsewhere, as desired, and preferably the lower end of conveyor 37 is immersed in the same liquid which serves to seal discharge port 35, the coke being thereby quenched before it is removed to the atmosphere.

When desired, a suitable spray arrangement, indicated at 38, may be provided to introduce water or other suitable cooling material onto the bed of coke at the discharge end of the conveyor to cause contraction of the coke and facilitate its removal from the conveyor. A suitable scraper 39 is also preferably provided to complete removal of the coke from the conveyor belt.

In an apparatus such as illustrated, and above described, the preferred range of operating conditions which may be employed to produce the desired results are approximately as follows: The relatively heavy oil to be coked may be supplied to furnace 6 either in relatively cool state from storage or in heated state direct from a cracking system, topping still or the like. Preferably, the oil is quickly heated in the furnace to a relatively high conversion temperature of the order of 900 to 1000° F., prior to its introduction into the separating zone preceding the coking stage of the system and the pressure employed during this heat treatment may range, for example, from a superatmospheric pressure of 30 pounds or less per square inch to 150 pounds or more per square inch. In order to assist quick separation of vapors and gases from the pitch-like residue following the heating step the separating zone is preferably operated at substantially atmospheric or relatively low superatmospheric pressure and substantially the same pressure is preferably employed in the coking zone. The bed of coke-like material is preferably heated, as it passes beneath the combustion chamber of the coking zone, to a temperature of from 1000 to 1500° F., or more, in order to insure the production of a low volatile, relatively dense coke of uniform quality and good structural strength.

As a specific example of the operation of the process as it may be accomplished in an apparatus such as illustrated and above described, the charging stock for the coking operation is a heavy residue of about 4° A. P. I. gravity derived from the cracking of a Mid-Continent topped crude of approximately 24° A. P. I. gravity. The cracking system is a well known type employing a heating coil and high-pressure reaction chamber connected in series and followed by a reduced pressure vaporizing and separating chamber, fractionating, condensing and collecting equipment with reflux condensate from the fractionator returned to the cracking coil. When operated without the coking step the cracking conditions in such a system may be controlled to produce approximately 60 per cent of good quality motor fuel and about 30 per cent of heavy residue of about 4° A. P. I. gravity. In the present case the temperature and pressure conditions employed in the cracking system are maintained substantially the same and the heavy cracked residue from the reduced pressure and separating chamber of the cracking system is passed through the heating stage of the coking system wherein it is quickly heated to a temperature of approximately 975° F. at a superatmospheric pressure of about 50 pounds per square inch, without allowing it to remain in the heating coil and succeeding separating zone for a sufficient length of time to permit any substantial formation and deposition of coke in these zones. The heavy pitch-like residue from the separating zone is discharged onto the conveyor and after being reduced to a coke-like mass by its contained heat and heat transmitted thereto from the refractory walls of the combustion chamber in the coking zone it is passed beneath the combustion chamber and heated at this point to a temperature of approximately 1300° F. The bed of coke at the discharge end of the conveyor is cooled by spraying with water, the resulting contraction causing it to loosen from the conveyor belt and it is removed therefrom in relatively large pieces, further quenched and discharged to storage. Vaporous products and gases from the separating zone and from the coking zone are subjected to condensation and the resulting condensate is returned to the reduced pressure vaporizing and separating chamber of the cracking system. By this operation the yield of gasoline from the cracking system is increased to approximately 70 per cent and when the total residual liquid from the vaporizing chamber is supplied to the coking stage the coke produced amounts to approximately 75 pounds per barrel of topped crude supplied to the cracking system. The only other product of the process is uncondensable gas. The coke produced is of exceptionally low volatility, uniform quality and good structural strength.

I claim as my invention:

1. A process for the cracking and coking of heavy hydrocarbon oils, which comprises quickly heating the oil to a high conversion temperature while passing the same in a continuous stream through a heating coil subjected to high rates of heating by heat radiated directly to its surface from materials undergoing combustion and the hot refractory confining walls, introducing the heated products into a separating zone wherein the resultant heavy pitch-like residue separates from their vaporous components, removing said vaporous components from the separating zone, subjecting the same to condensation and separating the resulting condensate and uncondensed gases, discharging said pitch-like residue from the separating zone onto the moving surface of a continuous conveyor within a coking zone causing the pitch-like residue to spread out in a relatively thin layer over the upper surface of the conveyor and reducing it thereon to a relatively thin mass of coke-like material by means of its contained heat and by means of heat radiated thereto from the relatively hot refractory walls which separate the coking zone from the combustion chamber, passing the coke-like material on the conveyor beneath said combustion chamber at which point coking and devolatilization of the coke to the desired degree is completed by heating the material on the conveyor to a high temperature by heat radiated directly to its upper surface from materials undergoing combustion in said combustion chamber and the hot refractory walls thereof, removing resulting combustion gases from said combustion chamber without permitting any appreciable quantity thereof to commingle with the hydrocarbon vapors and gases evolved within and separately removed from said coking zone outside said combustion chamber, and continuously removing the deposited bed of coke from the conveyor and quenching and discharging the same from the system.

2. A process for the cracking and coking of heavy hydrocarbon oils, which comprises quickly heating the oil to a high conversion temperature while passing the same in a continuous stream through a heating coil subjected to high rates of heating by heat radiated directly to its surface from materials undergoing combustion and the hot refractory confining walls, introducing the heated products into a separating zone wherein the resultant heavy pitch-like residue separates from their vaporous components, removing said vaporous components from the separating zone, subjecting the same to condensation and separating the resulting condensate and uncondensed gases, discharging said pitch-like residue from the separating zone onto the moving surface of a continuous conveyor within a coking zone causing the pitch-like residue to spread out in a relatively thin layer over the upper surface of the conveyor and reducing it thereon to a relatively thin mass of coke-like material by means of its contained heat and by means of heat radiated thereto from the relatively hot refractory walls which separate the coking zone from the combustion chamber, passing the coke-like material on the conveyor beneath said combustion chamber at which point coking and devolatilization of the coke to the desired degree is completed by heating the material on the conveyor to a high temperature by heat radiated directly to its upper surface from materials undergoing combustion in said combustion chamber and the hot refractory walls thereof, removing resulting combustion gases from said combustion chamber without permitting any appreciable quantity thereof to commingle with the hydrocarbon vapors and gases evolved within and separately removed from said coking zone outside said combustion chamber, commingling the last mentioned vapors and gases with those previously separated from the heated products in said separating zone, and continuously removing the deposited bed of coke from the conveyor and quenching and discharging the same from the system.

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