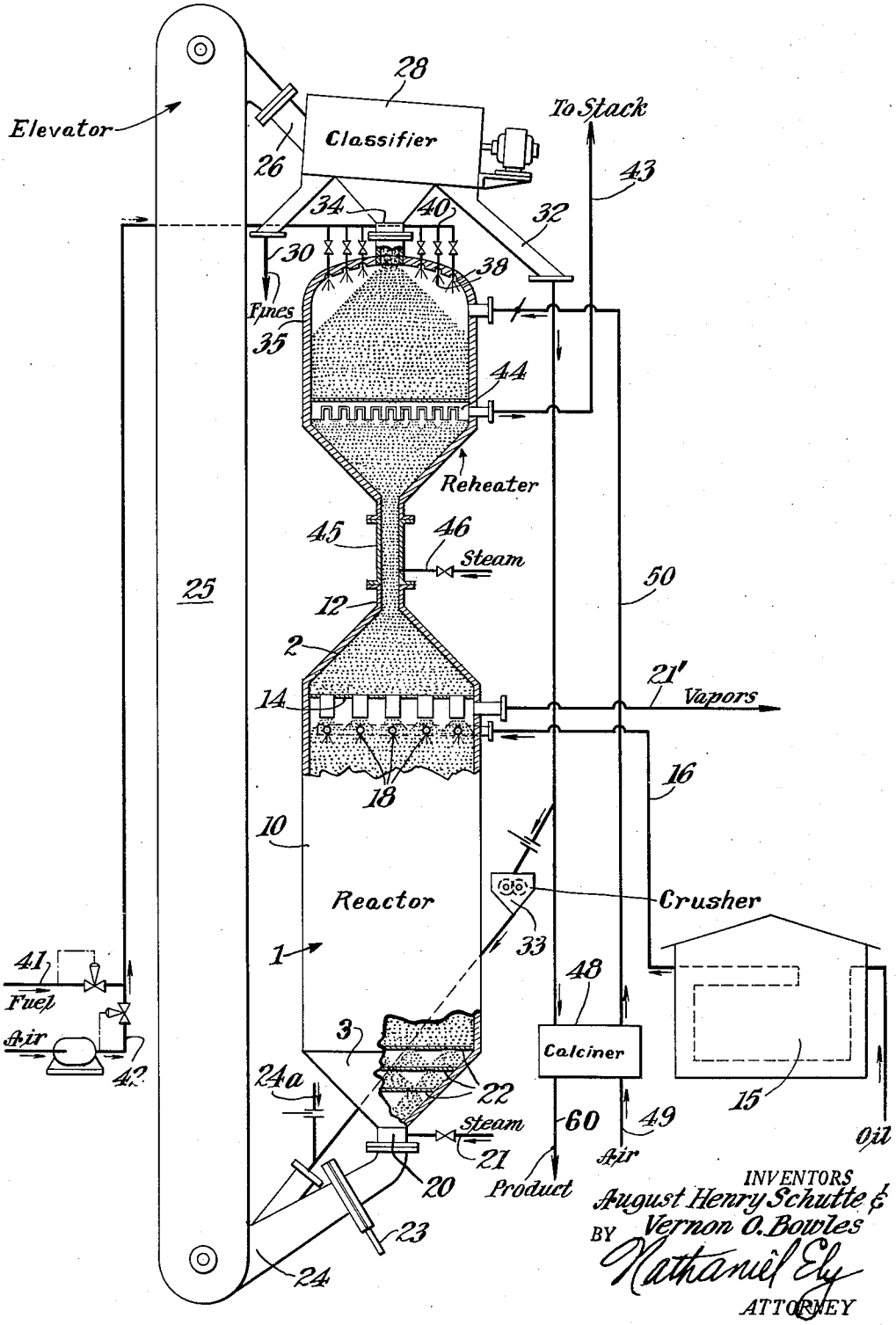
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HYDROCARBON CONVERSION

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HYDROCARBON CONVERSION

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6 Claims. (Cl. 202—14)

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This invention relates to an improved method of producing coke and is more particularly a continuation-in-part of our application Serial No. 510,119, filed November 13, 1943, and since abandoned in favor of application Serial No. 3,747, filed January 22, 1948, now Patent No. 2,561,334.

In accordance with our prior invention, we have disclosed a new method of producing coke by the continuous conversion of heavy hydrocarbons such as residues which are the by-products of crude oil distillation, or tars which are by-products of thermal cracking. The technique generally disclosed relates to the passage of a gravity packed column of discrete size particles of coke downwardly, solely by gravity, through a reaction zone and thence through a reheating zone, and then returning the particles to the reaction zone. In accordance with our disclosures, we have set forth certain conditions of operation which permit the complete drying out of a thin liquid coating applied to and carried by the coke particles during the continuous movement of the column downwardly, and when these conditions are met there is no adherence between particles of sufficient extent to interfere with the free flowing character of the column.

Our invention has also utilized the technique of avoiding the addition of heat to the coking operation except in the introduction of the preheated oil charge and the coke particles so that maximum temperature is at the top of the reaction zone and so that there will be no tendency of the vapors to condense as they move upwardly and are removed. There is also no dilution from products of combustion as air is excluded from the reaction zone.

In our prior applications it was contemplated that the reheating would be accomplished by introducing air into a sealed reheating zone with a partial combustion of some of the coke and the substantially complete freeing of the volatiles contained therein. While it was found that such operation resulted in a highly dense and superior form of coke, it has now been found that more effective and more economical control can be accomplished when only the removed net product is so calcined.

The present invention has for its principal object, the production of high quality calcined coke of dense nature containing substantially no ash and having a low volatile content.

A further object of the invention is to provide an improved method of calcining coke in a continuous contact coking unit whereby substantial heat economies are obtained by the handling of dry coke at elevated temperatures.

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It is an additional object of the invention to provide improved apparatus for controlling the size of the column particles and more efficiently reheating said particles in a continuous contact coking unit.

Further objects and advantages of our invention will appear from the following description of a preferred form of embodiment thereof taken in connection with the attached drawing which is a diagrammatic elevational view of the essential parts of a continuous contact coking unit for the production of calcined coke.

In accordance with a preferred form of embodiment of our invention, the reactor generally indicated at 10 is a suitable sealed vessel through which coke is continuously fed through the inlet 12 and is passed downwardly solely by gravity over the distributing baffle 14 adjacent which the liquid hydrocarbon charge introduced at 16 is distributed by the distributor elements 18. The oil is preferably heated to a suitable minimum temperature, as in heater 15, which aids in its partial vaporization in contact with the coke particles. These columnar flowing particles are maintained at a moderate temperature to accomplish a vaporization of a desired portion of the charge and the formation of a dry coke coating on the particles as they move downwardly to the outlet 20. This outlet may have a steam seal line 21.

It is our experience that a free flowing gravity packed mass can successfully carry and convert to dry coke and vapors up to about 50% of its weight of hydrocarbons of the residual type, where the discrete coke particles vary in size from as low as 5 mesh to ¾ inch in major dimension. It has been found important that the oil be so controlled as to form a thin film on the coke particles, and that the column of particles move through the reaction zone not only for a sufficient time but for a sufficient distance to prevent the liquid from running out the bottom and to assure the conversion of the particles to dryness. In general, a column height of at least 5 feet and preferably from 30 to 50 feet, depending upon the maximum temperatures allowable, is desirable. This contemplates that the temperature of the particles below the feed point is in the range of 900° to 1050° F. so that the resulting vapors which are collected under baffle 14 and discharged through the line 21' will be a near-virgin gas oil containing a minimum of olefins.

As the contact particles move through the reactor 10, uniform flow is necessary, which may be accomplished by flow control plates 22 of any well known type. Uniform flow assures evenness of charge distribution and uniform residence

time, it being known that the viscosity of the charge at the elevated temperature is about one tenth that of water. As the coating or particle growth thus is of the order of only 0.001 inch per pass, it will be apparent that repeated passage through the reactor is contemplated. This is accomplished by discharging the coated particles through outlet control valve 23 into elevator inlet 24, and, with any coke make-up from line 24a, into a suitable elevator 25 which carries the particles to the elevator outlet 26.

In accordance with our invention, we prefer to pass all of the contact particles into a classifier generally indicated at 28 which may be of any suitable type and which will discharge a uniform quantity of coke of desired size through line 34 for return to the system. Fines may be removed at 30 and the larger size particles removed as net product through line 32. If found desirable, some of this net product from line 32 may be passed through a crusher 33 and returned to the coke make-up line 24a for recycling.

Although the reaction is both exothermic and endothermic and nearly balanced in reactor 10 where the conversion is to dry coke, there is some heat loss by radiation and otherwise, and the particles which are to be returned to the reactor 10 are conveniently passed through the reheater 35. This is a separate sealed chamber connected with the classifier 28 through the inlet line 34. The upper part of the reheater 35 is provided with a series of radiant heat burners, generally indicated at 38, which are supplied by manifolds 40 with fuel gas from line 41 and air from line 42. The continuously changing surface layer formed by the coke particles as they enter the reheater 35 is thus continuously brought up to the desired temperature. Products of combustion flow downwardly and are discharged to stack line 43 from vapor collecting channel 44. The reheated coke particles then pass through seal pipe 45, having steam purge line 46, to the inlet 12 to the reactor 10, as previously mentioned.

We have found that the continuous and repeated passage of coke particles through the reheater and the reactor tends to create a highly dense, non-porous coke which appears to be radically different from the ordinary porous coal coke or petroleum coke known to the industry. To further improve the qualities of the coke product we find it desirable to pass it through the calciner 48 and subject it to controlled calcining with air introduced at 49. This novel product, which possesses great utility as a heat exchange medium and for metallurgical purposes, is described more fully and claimed in our copending application, Serial No. 46,168 filed August 25, 1948.

The coke normally leaving the classifier 28 through the outlet 32 is already in a highly heated condition, the temperature of which may range from 900° to 1,000° F., is substantially all of a size, and is, of course, completely free of any liquid. In the calciner 48 it is possible to rapidly bring the coke particles up to a temperature of 2,000° F. and the products of the combustion may be carried through the line 50 to the upper part of the reheater 35.

In view of the fact that the products of combustion leave the calciner 48 at approximately 2,000° F. they can be effectively used for reheating of the bed particles before they enter the reactor 10. In addition, the combustion gases are substantially cooled in their passage through the reheater 35 to the stack 43. It is of course understood that appropriate waste heat recovery means may also be used to aid in the cooling of the products of combustion.

In accordance with our present disclosure, we have effectively segregated the reheating and reaction zones and provided for the passage of the contact particle material through the elevator 25 while said material is in its coolest condition. The reduction in temperature at this point decreases the elevator operation cost. Furthermore only the net coke removed through the line 60 is calcined, with some economy in operation, thereby avoiding the need of high temperature operations in connection with all of the coke.

A typical unit for converting 18° A. P. I. Mid Continent reduced crude at the rate of 4500 bbl. per day, and producing major yields of dry coke will circulate from 200 to 300 tons per hour of contact material and the reactor may be approximately 16' in diameter with a 28' bed and the reheater may be approximately 16' in diameter and have a 14' column. With equilibrium coke the solids feed is from 9 to 15 times the oil feed by weight.

Inasmuch as calcining is largely for the purpose of removing volatile material, and only high temperatures are required, this may be accomplished either by combustion or by radiation from a suitable heat source. It is to be understood that either type may be used as conditions require. It is of course also possible to remove partially calcined coke directly from the system if the extra treatment is not required.

While we have shown and described a preferred form of embodiment of our invention, we are aware that modifications may be made thereto and we therefore desire a broad interpretation of our invention within the scope and spirit of the description herein and of the claims appended hereinafter.

We claim:

1. In a continuous, cyclic method of converting heavy hydrocarbons into coke and lighter hydrocarbons, the steps comprising continuously passing through a reaction space by gravity only, a relatively deep, compact, unagitated, free-flowing, homogeneous and continuous column of preheated coke particles, spreading on the coke particles of said moving column at points within said column and in an upper portion of said reaction space a charge comprising heavy hydrocarbons in liquid phase, converting the spread charge into solid dry coke adhering to the coke particles of said bed and vaporous lighter hydrocarbons, removing said vaporous hydrocarbons from said reaction space, recycling a substantially uniform quantity of said coke particles having solid dry adhered coke to a reheating space sealed off from said reaction space, continuously removing a net coke product corresponding in amount to the coke produced in the reaction space, calcining said net product coke in the presence of an oxygen containing gas, introducing the products of combustion from the calcining step into the reheating space to reheat the recycled coke particles therein, exposing the coke particles as they are fed into the reheating space to the heating effect of radiant heat burners, collecting and removing the products of combustion from the reheating space, and passing the reheated coke particles from the reheating space to the upper end of the reaction space while preventing the

flow of products of combustion from the reheating space to the reaction space.

2. In a continuous contact method of converting heavy hydrocarbon oils into coke and lighter hydrocarbons which comprises continuously and repeatedly passing a column of gravity packed preheated coke particles through a sealed reaction space solely by gravity, introducing a heavy hydrocarbon oil charge largely in liquid phase into the upper part of said coke column while so controlling the rate of movement of the column, the rate of feed of the charge per unit of column volume, the temperature of the entering coke particles and the distance through which the column moves before leaving the reaction space that the adhering liquid carried by the column particles will be converted to lighter hydrocarbon vapors and a dry, non-adherent coke coating on the particles, removing said lighter hydrocarbon vapors from the reaction space, discharging said coke coated particles from the reaction space, reheating and returning a substantially uniform quantity of coke particles to the reaction space, continuously removing a net coke product substantially equivalent to the amount produced by the conversion, subjecting the net coke product thus removed to a calcining operation in the presence of a gas, whereby the net coke product is raised to a substantially higher temperature than that in the reaction space, and cooling the gas from the calcining operation by contact with the said coke particles returning to the reaction space.

3. The method as claimed in claim 2, including the steps of classifying the dry coke coated particles discharged from the reaction space and removing the larger size particles as the net coke product supplied to the calcining operation.

4. The method as claimed in claim 3, including the step of bypassing a part of the removed larger size particles through a crushing operation to the reheating operation.

5. In a closed system for the continuous conversion of heavy residual oils into coke and lighter hydrocarbons by application of said oils to a gravity packed downwardly moving column of preheated coke particles, the combination comprising an upright reactor vessel having a particle inlet at its upper end and a particle outlet at its lower end, means for feeding heavy residual oil into the upper portion of the reactor vessel, means for withdrawing lighter hydrocarbons from the reactor vessel adjacent the oil feeding position, means for controlling the passage of coke particles through said particle outlet, an upright particle reheater chamber, said reheater chamber having a particle outlet at its lower end connected directly with the particle inlet of the reactor vessel, particle transfer conduit means extending between the particle outlet of the reactor vessel and the inlet of the particle reheater chamber, a product particle drawoff line in said transfer conduit means, a coke particle calciner of the combustion type connected in said particle drawoff line, and another line carrying the products of combustion from the calciner to the upper end of the particle reheater chamber, said reheater chamber being provided with means below said upper end for removing the products of combustion thus supplied.

6. In a closed system for the continuous conversion of heavy residual oils into coke and lighter hydrocarbons by application of said oils to a downwardly moving column of preheated coke particles, the combination comprising a vertical reactor vessel having an inlet at its upper end and an outlet at its lower end, means for feeding heavy residual oil into the upper portion of the reactor vessel, means for withdrawing lighter hydrocarbons from the reaction vessel adjacent the feeding position, valve means for controlling the passage of coke particles through said outlet, a vertical reheater chamber, said reheater chamber having an outlet at its lower end connected with the inlet of the reactor vessel, a particle classifier receiving all the coke particles discharged from the reactor vessel, said classifier being positioned above said reheater chamber and adapted to separate the coke particles passing from the reactor vessel into several sizes, a first line for feeding particles of a desired size from the classifier into the upper end of the reheater chamber, a second line for discharging particles of another size from the classifier for removal as product, a coke particle crusher, a valved line connected to the second line and including said crusher for recycling any desired portion of said particles of another size from the classifier to a point between the outlet of the reactor vessel and the inlet to the reheater chamber, whereby the particles thus recycled may be reduced to a suitable size for re-introduction to the system, a coke particle calciner of the combustion type connected in said second line beyond said valved line, and a third line for leading the hot gas produced in the calciner to the reheater chamber.

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