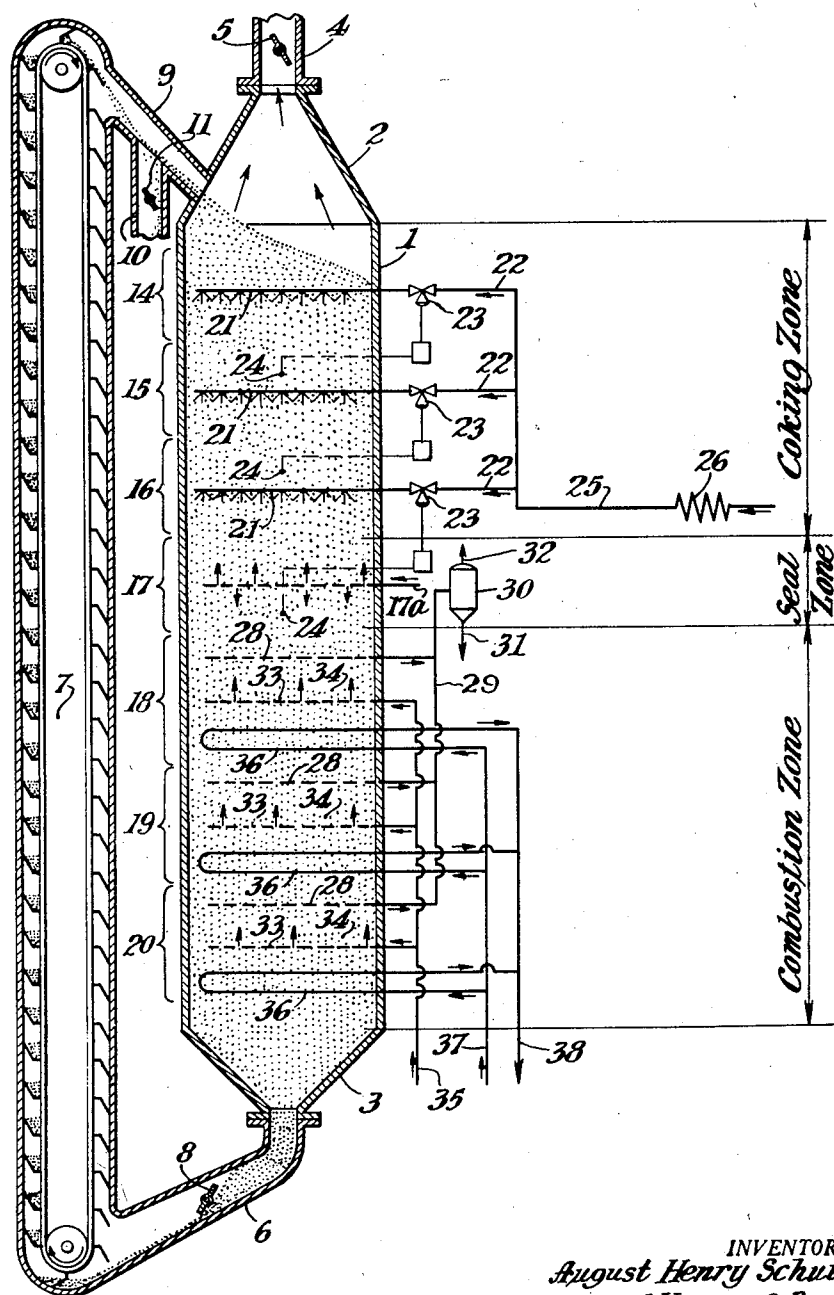


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METHOD OF HYDROCARBON CONVERSION TO
LOWER BOILING HYDROCARBONS AND COKE
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METHOD OF HYDROCARBON CONVERSION
TO LOWER BOILING HYDROCARBONS AND
COKE

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This invention relates to treating hydrocarbons and, in particular, to the treatment of hydrocarbons, residual oils and the like, such, for instance, as residues which are by-products of crude oil distillation, and tars, etc., which are by-products of thermal cracking. It is a continuation-in-part of our copending applications, Serial Nos. 510,118 and 510,119 filed November 13, 1943, both applications now abandoned.

It is a general object of this invention to provide a method of treating such heavy hydrocarbons or residual oils, etc. whereby to secure or recover the ultimate value of their components or fractions by thermally cracking or converting them to secure lighter components, vapors and/or gases, and coke.

A more specific object of the invention is to provide such a new and improved method of converting heavy hydrocarbons to vapors and coke which obviates the necessity for intricate, cumbersome, expensive and complicated coking equipment, such as coking drums and the like, with intricate, complicated, and relatively inefficient equipment such as cable, chain or hydraulic decoking systems for removing coke from the drums, by utilizing a moving continuous column of granular material such as coke as a heat carrying medium upon which the coke is deposited.

These and other objects and advantages of the invention will clearly appear from the following description thereof taken with the drawing, the figure of which is a schematic view with parts in section of a continuous reactor and regenerator.

The term "column" as herein used refers to a mass of gravity packed particles of contact material in substantial contact as distinguished from dispersed particles floated or in suspension in a stream or volume of liquid, gas or vapor.

According to the method of this invention, the charge of heavy hydrocarbons, such as residues or tars, supplied at a temperature below the point of complete vaporization, is spread or distributed through a moving column of preheated particles of suitable material, hereinafter referred to as contact material. This material may comprise a suitable cracking catalyst or an inactive or inert material such as particles of refractory material of suitable size, acting primarily as a heat carrying and coke deposit receiving media, or coke which may subsequently be used as fuel.

The charge spread on the particles of the heated column is subjected to cracking and coking whereupon coke is formed on the particles

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and the lighter hydrocarbons are drawn off as vapors and collected and/or further processed. For instance, they may be conveyed to a catalytic cracking unit of known type and therein converted into gasoline. The mild thermal conversion of the charge produces a large proportion of near virgin gas oil.

It is contemplated that the compact column will move downward solely under the influence of gravity at a substantially uniform rate such that each particle receives the same quantity of liquid and no flooding or gathering of pools of liquid occurs.

The depth of a coking zone unit which is the distance between applications of charge or between the application of charge and removal of the column from the coking zone, exceeds the lineal distance or drainage depth that the liquid portion of the charge will freely penetrate plus the distance the column moves during the reaction period. The residence time or the time that the average particle is in the column after application of charge is based upon the length of time required to completely flash off the vapors and convert the liquid residue to dry coke.

Continuous control of the rate of feed or input of charge in proper relation to the temperature and rate of movement of the column (i. e., volume of contact material through which a given quantity of residual oil is spread) prevents the clogging, gumming, or sticking together of the particles of the column which would render the apparatus inoperative or, at least, seriously impair the efficiency thereof. This control is a feature of this invention which is of great importance.

From the coking zone, the moving, unagitated particles with deposited residual carbon or coke pass freely downwardly through a sealing and purging zone where they are purged of residual hydrocarbon vapors, and thence through a combustion zone wherein a part or all of the coke may be burned, a part of the heat being used to reheat the particles and the balance of heat being withdrawn by heat exchange. Thereafter a uniform quantity of contact material is continuously returned to the coking zone as preheated column make-up to complete the cycle.

The particles of contact material of the column with adhering coke are subjected to combustion at temperatures which are limited only by the character and properties of the contact material with the object of converting the coke to heat. If the contact material be inert refractory material, for instance, it is merely necessary that

the temperature in the coke burning or combustion zone be below the temperature of fusion thereof. If the contact material be a cracking catalyst, it is necessary that the maximum temperature in the coke burning or combustion zone be limited to prevent overheating with resultant damage to the adsorptive structure of the catalyst particles. The gaseous and fine solid products of this combustion are withdrawn and separated by a gas solids separator, for instance, and collected, as desired.

The heat energy liberated by the combustion or coke burning may be collected in a suitable heat exchange medium contained in heat exchange means disposed in the path of the column and conveyed from the heat exchange means to any desired station for use. For instance, the heat exchange medium may be boiler feed water, and steam formed in the heat exchange means by the heat of burning or combustion in the combustion zone may be piped to the water drum of a boiler or the like. Likewise, this heat exchange medium may comprise molten salt or other media especially adapted to the particular heat exchange problem.

If the contact material is coke, the particles may be calcined or freed of the greatest part of their volatile content, by heat of combustion of a small portion of the coke mass, the net coke production being drawn off as dry, calcined or partially-calcined coke product, and the balance returned to the coking zone.

Illustrative apparatus for accomplishing the principles of this invention is shown diagrammatically in the drawings. The kiln or unit therein shown is of a type well known in the art as the "Thermoform kiln" and comprises a vertical shell having a main portion 1 of either rectangular or circular cross-section, an upper convergent end 2 and a similar lower convergent end 3, together forming a reaction space or chamber 1, 2, 3. Leading from the upper end 2 is a vapor or gas discharge outlet 4 provided with a valve 5 for controlling the discharge of gases and/or vaporous products of the reaction carried out in the upper portion of the reaction space or chamber 1, 2, 3. The outlet 4 may, for instance, be connected with a unit of the type known in the art as a "Thermoform catalytic cracking unit" for conversion of these vaporous products into gasoline.

Connected with the lower convergent end 3 is the inlet 6 of elevator 7, which inlet is provided with an adjustable gate or valve 8 for controlling egress of contact material from the sealed reaction space or chamber 1, 2, 3. The elevator 7 is of conventional type, being provided with an endless bucket chain supported on a pair of sprockets, at least one of which sprockets is driven in a conventional manner. Leading from the upper end of the housing of the elevator 7 is the elevator outlet duct 9 which extends into one side of the convergent shell end portion 2.

As shown in the drawing, the continuous moving column comprising particles of contact material, substantially fills the main portion of the sealed reaction space or chamber 1, 2, 3 and moves uniformly therethrough by gravity alone at a rate controlled by the gate or valve 8. The preferred operation is such as to maintain a substantially constant maximum inventory of particles in the reaction space considering the natural angle of repose of the particles. The space or chamber 1, 2, 3 is divided generally into a coking zone at the upper end, an intermediate sealing and purging zone therebelow, and a reheating,

combustion and steam generating or calcining zone at the lower end of the interior thereof. The coking zone is designated 14, 15, 16 inasmuch as it comprises three similar units or reaction spaces 14, 15 and 16 superposed one above the other as shown in the drawing. The sealing and purging zone is designated 17. The combustion and steam generating zone is designated 18, 19, 20 inasmuch as it comprises three similar superposed units or reheating spaces 18, 19 and 20, as shown in the drawing.

Each of the reaction spaces 14, 15, and 16 of the coking zone is provided with residual oil charge feeding and spreading means comprising, for instance, a sparger 21 connected with a supply pipe 22 preferably having therein a thermostatic valve 23 controlled by a thermostatic element 24. Each thermostatic element 24 is suitably located in the reaction space to make the rate of supply of the charge, under the control of each valve 23, responsive to the temperature in its respective coking zone. Valves 23 may, of course, be manually controlled. Each of the supply pipes 22 is connected with a common supply line 25 leading from a suitable supply of heavy hydrocarbon charge material as, for instance, residual oil, "bottoms" or tars.

The spargers 21 are constructed and arranged in a manner to uniformly distribute the oil over all of the particles. While the spargers 21 discharge the oil in a substantially concurrent direction with respect to the column, the oil initially tends to drain between the particles until it reaches some point at which the oil moves downward with the particles, thereafter being carried by the particles. Preferably the feed is below the top of the column so that the column tends to act as an entrainment separator, as well as preventing deposit of coke on the wall of the chamber. The depth of feed below the top of the column controls the amount of thermal cracking of the vapors passing through the column.

A heat exchange unit, such as heater 26, may be provided in the supply line 25 to control the temperature of the charge admitted through the respective spargers 21 to their respective spaces or units of the coking zone, i. e., to heat it when necessary, to an admission temperature below the temperature of complete vaporization of the charge.

The sealing and purging zone 17 merely provides a seal between the coking and combustion zones and is provided with means for purging the particles and deposited coke of residual hydrocarbon vapors. This latter means comprises a distributor 17a connected with any suitable source (not shown) of steam or purge gas. The purge gases will flow out through the adjacent collector 28 with the combustion products from calcining as well as upward with the vapors.

Each of the units or spaces 18, 19, and 20 of the combustion and steam generating zone is provided adjacent its upper end with a collector or collector element 28. Each of these collectors or collector elements through which gases and fine particles of combustion by-products are withdrawn from the combustion or coke burning zone of the reaction space 1, 2, 3 has a common connection with suitable collecting means as, for instance, with the intake 29 of the gas-solids separator 30.

While this gas-solids separator 30 may be of any suitable type, it is shown, for purposes of illustration, as a "Cyclone" separator having a delivery outlet 31 for solids and a delivery out-

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let 32 for combustion gases. While its use is generally desirable, it may be omitted when the case is otherwise.

Below and spaced from each collector or collector unit 28 is an air distributor 33 which supplies air for combustion in the burning section 34 of each combustion unit. This burning section of each combustion unit comprises the space between each air distributor and the collector 28 thereabove. Each of the air distributors 33 is connected with a common air supply line 35 leading to a suitable source (not shown) of air or gas or other suitable combustion medium.

Below and spaced from each air distributor 33 is a coil or unit 36 forming a heat exchange or steam generating unit, each unit 36 being connected with a common inlet or supply line 37 for boiler feed water or other heat exchange medium and also with a common return line 38 extending, for instance, to the water drum of a boiler or the heater 26 for utilizing the heat energy stored in the water or formed steam or other heat exchange medium such as molten salt or the like passing through the coils or heat exchange units 36. Also the residual oil charge feed may pass directly through these coils for heating the charge, if desired. The space adjacent each coil or heat exchange unit 36 comprises the steam or heat energy generating section of that unit of the combustion zone. The lowermost heat exchange element 36 provides for close control of the temperature of the reheated mass passing out of the lower end of the combustion zone into the elevator inlet 5.

While the coking zone is illustrated as comprising three coking units and the combustion and steam generating zone is illustrated as comprising three units, it is of course to be understood that these zones may comprise a single unit or any number of units, depending upon the particular circumstances and materials to which the method of this invention is adapted.

The temperature of the charge, i. e., residues or tars, supplied through the spargers 21 is controlled through the heater 26 in the customary manner. The rate of supply of the charge is controlled, according to the temperature of the reaction spaces below the feed point. This may be accomplished by the thermostatic elements 24 and valves 23 or the valves 23 may be manually controlled.

The rate of travel of the column through the unit as well as the introduction of particles to the unit is controlled by controlling the gravity removal of the particles through the adjustable gate or valve 8. Uniform flow of the particles is normally possible with an outlet of large enough size with respect to column diameter to avoid channelling. If, however, it is not feasible to make the outlet large enough, proportioned opening flow control plates or tubes characteristic of "Thermoform" kins and shown in Evans Patents 2,389,493 and 2,412,135 or equivalent may be used in the convergent section 3. The discharge through valve 8 is homogeneous.

In known commercial coking methods, the heat energy required by the coking and conversion reaction is supplied at the expense of the sensible heat of the charge. In our method, however, the major part of such required heat energy is supplied from the sensible heat of the preheated particles which may be heated by combustion of the carbon deposit. The remainder of the heat energy is supplied from the sensible heat of the

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charge admitted through the spargers. This is a much smaller and less important portion of the heat energy required by the conversion and coking reaction.

Addition of heat energy to the sensible heat of the particles occurs in the coke burning zone or space through burning of the coke. Where, as is contemplated, the heater 26 is operated from one or more of the coils or heat exchange elements 36, or where the charge is passed directly through one of the coils or elements 36, addition of heat energy to the sensible heat of the charge admitted to the coking zone or space, also is accomplished through coke burning.

The temperature in the combustion zone may be controlled by regulating the admission of air to the burning sections and by control of the heat exchange units or elements 36. The lowermost element 36 provides means for controlling the temperature of the contact material leaving the combustion zone 18, 19, 20 for return to the reaction space by the elevator 7, as well as the temperature of its readmission through the elevator outlet 9.

The following is an illustrative operative cycle of the above described apparatus, according to this invention.

Operation

The particles of contact material re-introduced through the elevator outlet 9 to the reaction space 1, 2, 3, above the coking zone 14, 15, 16 are preheated, since they were discharged hot from the lower end of the reaction chamber below the combustion zone 18, 19, 20 into the elevator inlet 6 at a temperature controlled by the lowermost heat exchange element 36.

The spreading of the residual oil or heavy hydrocarbon charge on these preheated particles of contact material by the spargers 21 in the coking zone is accompanied by cracking of the charge into lighter hydrocarbons in vapor form and formation of coke adhering to the particles of contact material in the moving column. The lighter hydrocarbons in gaseous or vaporous form pass upwardly through the portion of the column in the coking zone. The particles and deposited coke pass thence to the sealing and purging zone.

The sealing and purging zone 17 by reason of the supply of steam or purge gas through the unit 17a prevents vapor flow between the coking zone 14, 15, 16 and the combustion zone 18, 19, 20. From the sealing and purging zone 17, the particles and adhering coke pass through the three burning sections 34 of the combustion zone 18, 19, 20, where the temperature is limited only by the type of contact material of the column as pointed out above. The temperature is sufficiently high to burn off all the coke formed in the coking zone and adhering to the particles, or to burn the desired amount of coke where coke on coke is formed, the combustion gases and fine solid particles being collected by each collector 28 and carried through the intake 29 to the separator 30, where such separator is provided. In the separator 30, they are separated for collection of solid particles.

The excess heat generated by this burning or combustion is absorbed by the heat transfer medium or, in some cases the charge, passing through the heat transfer coils or elements 36 for use externally of the reaction space 1, 2, 3 as pointed out above. Thus, the products of catalysis formed in the reaction chamber above the

coking zone 14, 15, 16, if catalysis occurs, and the vaporous products of cracking in the coking zone 14, 15, 16, are withdrawn through the discharge outlet 4 for further separation, processing, or collection, and the coke formed in the coking zone 14, 15, 16 is all burned off the particles in the combustion and steam generating zone 18, 19, 20.

The hot particles are withdrawn from the lower end of the reaction chamber 1, 2, 3, as a free flowing stream and returned by the elevator 7 through the elevator outlet 9 to the upper end of the reaction chamber above the coking zone 14, 15, 16 whereby the cycle is made continuous, the moving particles being used over and over in the process.

The use of coke as the particle material is of particular advantage under certain circumstances. The recycled coke is extremely hard and effectively withstands the attrition in its movement in the reaction and reheating cycle, and the excess coke can be drawn off and used for fuel in other than the combustion chamber. The drawing illustrates the manner of drawing off net coke production, dry and calcined, through an outlet 10 in the elevator outlet duct 9. Valve 11 controls this drawing off. The coke formed can be readily burned with no danger of destruction to the particles and except for the increase or decrease in the size of the particles, it makes little difference whether or not more or less coke burned.

Inasmuch as the nature of the particles may also include other materials than those above mentioned, the inclusive or comprehensive term "contact material" as used herein is of substantial scope since it covers the three rather divergent types of coke deposit receiving media, i. e., cracking catalyst material, chemically inert refractory material, or coke whether of petroleum or other origin. Specifically, these may include non-porous material as dense as beach gravel or porous materials including "Koppers" coke, alumina, "Carborundum," porous crushed fire brick, porous ceramic particles as well as spent cracking catalyst particles or beads. Such porous materials may have a bed particle porosity from 5% to 50% by volume, i. e. for a given unit of gross volume in any discrete particle from 5% to 50% of that volume would represent pore volume. In addition, the column itself, when comprised of non-porous material such as round beach gravel of five mesh, will have voids of approximately 40%.

The contact time which is synonymous with reaction time, according to the method of this invention, is the time required to convert the liquid portion of the hydrocarbon charge to dry coke under the conditions of operation. It is dependent upon the temperatures of admission of the charge and of the column material as well as the properties of the charge and the types and relative quantities of the end products desired. The residence time of the particles in the reactor is at least sufficient to provide adequate reaction time and in general, with heavy reduced crudes, it is at least 5 minutes, and it may be as much as 30 minutes or more before the coke deposited on the particles is dry and non-tacky so that the particles may be removed as a free flowing homogeneous stream through the restricted discharge conduit 6. Maintaining proper time, uniform travel and proper feed and temperature rates will prevent formation of clumps in the column due to the cementing together of

the particles and the column will now freely, solely by gravity, throughout the reaction zone.

The spread density of the feed will vary with the amount of the feed which does not immediately vaporize upon contact with the hot column particles as well as the porosity of the column. The liquid portion of the feed that passes downwardly with the column must not exceed the carrying capacity of the discrete particles so that the hydrocarbon does not discharge as a liquid from the bottom of the reaction space. We find that the range of charge varies from about 5% to about 50% by weight of solid column material passing the feed point. This may be expressed in terms of a unit of 100 tons per hour circulating rate as 1000 to 10,000 bbl./day of charge.

It has been found that the best results are obtained when the temperature of the column below the hydrocarbon feed point is maintained in the range of 850° F. to 1050° F. The particle inlet temperature, the rate of flow of the column, the temperature and rate of feed of the hydrocarbon charge are, therefore, jointly adjusted to maintain this predetermined temperature.

The yield per pass or cycle may be greatly increased by applying the liquid hydrocarbon to the granular material in the reaction space as a multiplicity of superimposed envelopes or coatings, each individually relatively thin but collectively of substantial thickness. This "Multiple Coating" is effected, according to this invention by dividing the coking zone into a multiplicity of vertically spaced reaction areas or units wherein the simultaneously applied charge feeds and/or spread densities are independently controlled, according to the temperature of the material in each zone, or by repeatedly recycling the particles through the reaction spaces.

It is much easier to secure a dry coating when the thickness thereof is slight, and since the dryness or non-tacky nature of the deposited coke is important in preventing the formation of lumps, clumps and cementing in the column, the above described "multiple coating" principle is an important feature of this invention. The coatings secured on the particles or nuclei are dry, non-tacky, and brittle, whereby the movement of the column is sufficient to maintain the coated particles separate from one another, or discrete within the column, without necessity for the provision of mechanical agitation or stirring.

The particle size for uniform operation should not be of too broad a range and while we prefer to limit the range from about $\frac{1}{8}$ " to $\frac{3}{4}$ " major dimension, we have operated with as low as 50 mesh and as large as $1\frac{1}{2}$ ". We also find that the particles "grow" or increase in size by about .001 inch coating per pass.

A specific example is as follows:

Charge.—Mid Continent reduced oil, with A. P. I. gravity @ 60° F. of 18.0:

Flash Point, C. O. C., 330° F.

Fire Point, C. O. C., 435° F.

Pour point, 80° F.

Particle material.—Round stone gravel (inert refractory):

Size: Average approx. 5 mesh (U. S. Std. Sieve size).

Apparent density: 1.549 g./cc., or approx. 97 lbs. per cu. ft.

Particle density: 2.63 g./cc.; particle porosity approx. zero.

Column voids: 41% approx.

Procedure.—6.7 lbs. of (oil) charge was introduced at 840° F. to the coking chamber; spread upon 24 lbs. of particle material at 970° F. Contact time 8 minutes, 36 seconds:

Temperature of the oil fell from 840° F. to 838° F.

Temperature of the particle material fell from 970° F. to 870° F.

The products comprised:

Gas, 0.186 lb. or 2.8%

Distillate, 5.750 lb. or 86.9%

Coke, 0.500 lb. or 7.5%

Further investigation indicated the preferred range for the same oil charge to be as follows:

The oil charge introduced into the coking chamber at 800° F. to 900° F. and contacted with a column of contact material comprising chemically inert refractory particles as above at 900° F. to 1100° F. providing the main portion of the coking heat or thermal energy per 100 lb. of refractory material and contact time of 5 min. to 30 min. will produce a coke yield of 3 lbs. to 30 lbs. of coke per 100 lbs. of oil charge introduced.

An example of the application of a heavy hydrocarbon to a continuously moving petroleum coke particle mass is as follows:

Charge.—18° A. P. I. Illinois crude:

Ramsbottom carbon, 8.6 weight per cent

20% distillation temp.¹ 775° F.

50% distillation temp.¹ 985° F.

Particle material.—Dense petroleum (equilibrium) coke:

Size: average, $\frac{1}{8}$ to 1" maximum length.

Apparent density: 0.89 g./cc., or approx. 60 lbs. per cu. ft.

Particle density: 1.39 g./cc.; particle porosity approx. .03.

Column voids: 34% approx.

Procedure.—49 bbls. per day of oil charge was introduced at 795° F. to the coking chamber; through which 9000 pounds per hour of coke was passed. (Oil-solids ratio was 13:1.) Particle inlet temperature was 1040° F. and the temperature of the column below the feed point was 1005° F.

The particles in the column moved downwardly from the feed point for a distance of approximately 5.0 feet before reaching the bottom of the conversion zone and the average particle residence time was approximately 30 minutes to allow a full and complete conversion. The coke was removed as a free flowing homogeneous stream.

The foregoing examples are illustrative of the operational features of our process but are not to be considered limiting thereof and we desire to comprehend within our invention such modifications as are included within the scope of the following claims.

We claim:

1. In a method of converting heavy hydrocarbons into coke and lighter hydrocarbons, passing through a space including a reaction zone and a combustion zone by gravity only, a relatively deep, 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 zone a charge comprising heavy hydrocarbons in liquid phase injected in a direction concurrent with the direction of column movement, converting the spread charge into solid coke adhering to the coke particles of said column and vaporous lighter hydrocarbons removable from said reaction zone, subjecting said coke particles and adhering coke to partial combustion in said combustion zone which is sealed off from said reaction zone to drive off volatiles from the coke formed in said reaction zone and adhering to the coke particles of said column, and removing from the portion of said column in the zone of partial combustion sufficient heat to bring said portion of the heated column of coke substantially to a temperature suitable for readmission to said reaction zone as column make-up, the products of combustion being prevented from entering into the reaction in said reaction zone by the sealing off of said reaction zone from the combustion zone in which partial combustion occurs.

2. The method as claimed in claim 1 in which the net coke produced is drawn off as dry calcined coke after said partial combustion and the balance of the particles not drawn off is returned to the upper portion of the reaction zone.

3. The method of converting residual hydrocarbons into dry carbon residue and lower boiling hydrocarbon vapors in the presence of a particle form solid contact mass, which comprises preheating the particles of said contact mass, continuously moving the contact mass in said preheated condition uniformly downwardly through a sealed reaction space as an unagitated gravity packed column, preheating the residual hydrocarbon charge to a temperature of about 800° F. but below the temperature of incipient coking and not above the desired temperature of reaction, applying the preheated charge comprising residual hydrocarbons substantially in liquid phase to said particles in the upper part of said reaction space so that the initially unvaporized portion of the charge will move in a direction concurrent with the direction of column movement, mutually adjusting the inlet temperature of said contact particles to the reaction space, the temperature of said preheated hydrocarbon charge, the rate of application of said preheated hydrocarbon charge and the rate of flow of said column of contact particles to maintain a predetermined reaction temperature of between about 850° F. and about 1050° F. in said reaction space below the point of application of said charge, retaining the particles of said moving column in said reaction space after said application of charge and without other addition of heat or further charge application for at least five minutes and for a time sufficient to complete conversion of the said charge to lower boiling hydrocarbon vapors and non-agglomerating column particles having a dry carbon deposit thereon, withdrawing lower boiling hydrocarbon vapors countercurrently through said column and discharging said vapors from an upper portion of said reaction space, continuously and uniformly withdrawing the solid contact mass as free flowing discrete particles from the reaction space by a controlled gravity flow without agitation or application of mechanical force, and sealing the removal of the particles from the reaction space against loss of hydrocarbon vapors therefrom.

4. The method of treating residual hydrocar-

¹ Vacuum distillation corrected to atmospheric pressure.

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bons to remove carbonaceous residue therefrom and to produce lower boiling hydrocarbon vapors, which comprises continuously passing solid particles of free flowing coke contact material repeatedly through a confined path including a conversion zone and a reheating zone, through which said particles move downwardly in the form of a continuous gravity-packed column, and a return conduit, preheating the residual hydrocarbon to a temperature of about 800° F. but below that of incipient coking, applying said preheated charge comprising residual hydrocarbons in liquid phase to the particles of said column at the upper part of said conversion zone so that the charge will move in a direction concurrent with the direction of column movement, mutually adjusting the inlet temperature of said contact particles to the conversion zone, the temperature of said preheated hydrocarbon, the rate of application of said preheated hydrocarbon charge and the rate of flow of said column of contact particles to maintain, without other addition of heat, a temperature in said column within the conversion zone of between about 850° F. and about 1050° F., retaining the particles of the moving column in said conversion zone after said application of charge and without other addition of heat or further charge application for at least five minutes and for a time sufficient to produce a mild liquid phase conversion of the liquid portion of said preheated hydrocarbon into lower boiling hydrocarbon vapors and a dry carbonaceous deposit on said contact particles, continuously removing said lower boiling hydrocarbon vapors from the conversion zone, said contact particles with said dry carbonaceous deposit thereon continuously moving as a free flowing homogeneous stream without application of mechanical force from said conversion zone and thence continuously moving said particles into the reheating zone, substantially preventing the escape of hydrocarbon vapors therewith, reheating said contact particles in the reheating zone, and removing said reheated contact particles from the reheating zone and replenishing said column at the upper part of said conversion zone with reheated contact particles to maintain a substantially constant inventory of contact particles therein while substantially preventing entry of gases into said conversion zone.

5. In a method of converting heavy hydrocarbons into coke and lighter hydrocarbons, passing through a space including a reaction zone and a combustion zone by gravity only, a relatively deep, unagitated, free-flowing, homogeneous and continuous column of preheated coke particles of contact material, spreading on the coke particles of said moving column at points within said column and in an upper portion of said reaction zone a charge comprising heavy hydrocarbons in liquid phase so that the charge will move in a direction concurrent with the direction of the column movement, converting the spread charge into dry solid coke adhering to the coke particles of said column and vaporous lighter hydrocarbons removable from said reaction zone, subjecting said coke particles and adhering coke to partial combustion in said combustion zone which is sealed off from said reaction zone to reheat the coke and to drive off volatiles from the coke formed in said reaction zone and adhering to the coke particles of said column, and removing from the portion of said column reheated in the zone of partial combustion sufficient heat to bring said portion of the heated

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column of coke substantially to a temperature suitable for readmission to said reaction zone as column make-up, the products of combustion being prevented from entering into the reaction in said reaction zone by the sealing off of said reaction zone from the portion in which partial combustion occurs.

6. In a method of converting residual hydrocarbons into coke and lighter hydrocarbons, the steps of passing through a closed space including a reaction zone and a combustion zone by gravity only, a relatively deep, unagitated, free-flowing, homogeneous and continuous column of particles preheated to a temperature in the range of 900° F. to 1100° F.; spreading on the particles of said moving column at points within said column and in an upper portion of said reaction zone a charge comprising residual hydrocarbons in liquid phase and below the temperature of incipient coking so that the initially unvaporized portion of the charge will move in a direction concurrent with the direction of column movement; retaining the particles of the moving column in said reaction zone after said charge spreading and without other addition of heat or further addition of charge for at least five minutes and for a time sufficient to convert the initially unvaporized portion of the charge into solid coke adhering to the particles of said column and vaporous lighter hydrocarbons solely by the heat supplied by preheated particles; removing the vaporous lighter hydrocarbons from the upper portion of said column in the reaction zone; sealing off the reaction zone from the combustion zone whereby volatile material is prevented from passing with the particles into the combustion zone; subjecting said particles and adhering coke to partial combustion in the combustion zone to burn off the coke formed in said reaction zone and adhering to said particles, and to bring the particles of said column in the combustion zone substantially to a temperature suitable for readmission to said reaction zone as column make-up, the products of combustion being prevented from entering into the reaction in said reaction zone by the sealing off of said reaction zone from the combustion zone in which partial combustion occurs; and returning a substantial proportion of the reheated particles back to the reaction zone in a vapor tight path.

7. In a closed continuous and cyclic method of converting residual hydrocarbons into coke and lighter hydrocarbons, the steps comprising passing through a space including a reaction zone and a reheating zone by gravity only, a relatively deep, unagitated, free-flowing homogeneous and continuous column of preheated particles at a temperature in the range of 900° F. to 1100° F.; spreading on the particles of said moving column at points within said column and in an upper portion of said reaction zone a charge comprising residual hydrocarbons substantially in liquid phase and below the temperature of incipient coking so that the initially unvaporized portion of the charge will move in a direction concurrent with the direction of column movement; retaining the particles of the moving column in said reaction zone after said charge spreading and without other addition of heat or further addition of charge for at least five minutes and for a time sufficient to convert the initially unvaporized portion of the charge into dry solid coke adhering to the particles of said column and vaporous lighter hydrocarbons solely by the heat supplied by the preheated particles;

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removing the vaporous lighter hydrocarbons from the upper portion of said moving column in the reaction zone above the points of charge spreading; reheating said particles and adhering coke in said reheating zone while substantially preventing gaseous flow between said reaction and reheating zones; controlling the reheating of said particles in the reheating zone to bring said heated particles substantially to a temperature suitable for readmission to said reaction zone as column make-up; and recycling said reheated particles to the upper portion of said reaction zone.

8. The method of converting a charge of heavy hydrocarbons into dry carbon residue and lower boiling hydrocarbon vapors in the presence of a particle form solid contact mass of coke, which comprises preheating the particles of said contact mass to a temperature above the desired reaction temperature and in the range of about 900° F. to about 1100° F., moving the contact mass in said preheated condition downwardly through a sealed reaction space as an unagitated, gravity packed column, applying the charge at a temperature below the temperature of incipient coking and comprising heavy hydrocarbons in liquid phase to the particles of said moving column at a point within said column and at the upper part thereof so that the initially unvaporized portion of the charge is taken up by and is moved downwardly with the particles as a wetting film, mutually adjusting the inlet temperature and rate of flow of said contact particles and the temperature and the rate of flow to the charge of the reaction space so as to maintain a predetermined reaction temperature of between about 850° F. and about 1050° F. in said reaction space below the point of application of said

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charge, retaining the particles of said moving column in said reaction space after said application of charge and without other addition of heat or further charge application for at least five minutes and for a time sufficient to complete conversion of the said charge to lower boiling hydrocarbon vapors and coke particles having a dry non-agglomerating, carbon deposit thereon, withdrawing lower boiling hydrocarbon vapors from said reaction space, and separately withdrawing the particles bearing dry carbon deposit from said space as a free flowing stream without the application of mechanical force.

9. The method of converting the residual hydrocarbons as claimed in claim 3 in which the particles of contact material are coke and the particles withdrawn from the reaction space are circulated through a closed reheating space wherein the particles are reheated to a temperature sufficient to supply the heat of reaction, and are then returned in closed circuit to the reaction space.

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