

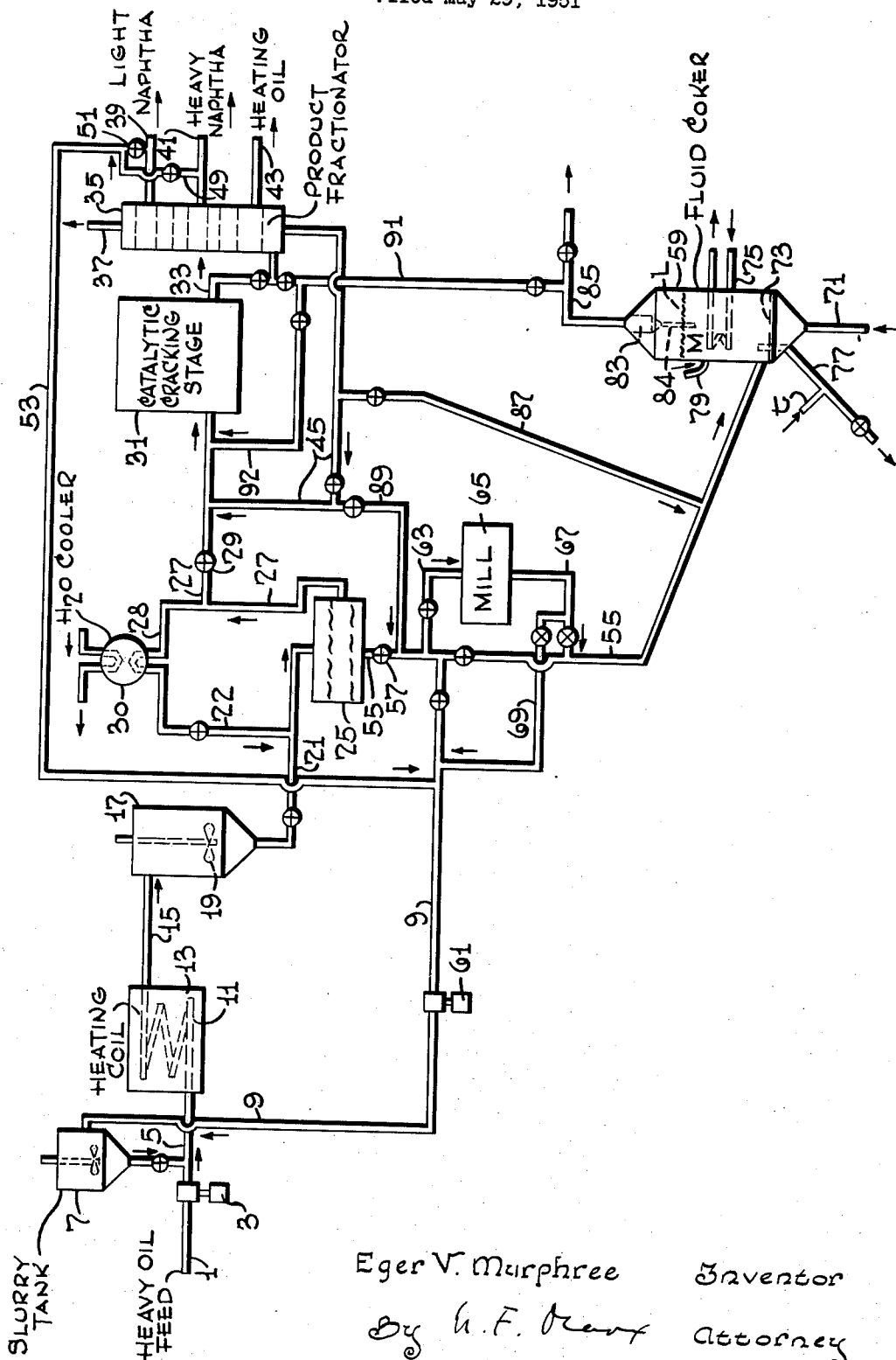
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COKING OF HYDROCARBON OILS

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COKING OF HYDROCARBON OILS

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The present invention relates to a method of treating hydrocarbons. More particularly, the invention pertains to an improved process of converting heavy hydrocarbonaceous residues, such as topped or reduced crudes, pitches, asphalts or the like, into lower boiling more valuable hydrocarbons, such as gasoline and heating oils. The improvement of the invention resides in the combination of steps involving the heat-soaking or thermally cracking of heavy residual oil in liquid phase under conditions conducive to the formation of gas oil suitable for subsequent catalytic cracking, the separation of the entire effluent of the heat-soaking stage by settling into a clarified oil and a coke-containing slurry, the catalytic cracking of the clarified oil, and the coking of the slurry.

It has been proposed to dilute heavy residual oil feed with a light distillate oil and then coke the diluted feed in the presence of subdivided solids at low temperatures to maintain the mixture in the liquid phase during coking. Such a process is disclosed and claimed in the copending Kimberlin and Gray application Serial No. 226,893 filed May 17, 1951. The present invention involves an improvement in processes of the type just described.

Low temperature liquid phase treatment of the character referred to above has for its principal purpose the production of hydrocarbon oils of suitable boiling range and quality for a conversion into high octane motor fuels by subsequent catalytic cracking. Prior to the present invention it has been proposed to subject the effluent of the liquid phase cracking treatment to fractionation to recover, in addition to small proportions of gas, gasoline and heating oils, substantial yields of gas oils suitable for catalytic cracking, and coke-carrying liquid bottoms which may be further treated to separate the coke from the bottoms. A part of the coke may be returned to the liquid phase coking stage as seed coke. The liquid bottoms may likewise be recycled and further converted. In many cases, a simpler and less expensive procedure may be desirable for working up the coker effluent. Also, the conversion of liquid phase cracked products boiling above the gas oil range into valuable gasoline and additional gas oil is of considerable interest. The present invention provides a procedure suitable for these purposes.

It is, therefore, the principal object of the present invention to provide an improved process for converting heavy residual oils into gasoline and other light distillate fractions. Other and more specific objects and advantages will appear from the following description of the invention wherein reference will be made to the accompanying drawing, the single figure of which is a semi-diagrammatical illustration of a system adapted to carry out a preferred embodiment of the invention.

In accordance with the present invention, a heavy crude residual oil from vacuum or atmospheric distillation of crude petroleum or other heavy stocks of similar composition is initially subjected to mild thermal liquid phase cracking at temperatures of the order of from 750°–900° F. for a period sufficient to convert a substantial portion

of the feed into intermediate fractions including gas oil. This treating operation is preferably carried out in the presence of a small amount of added coke or other solid particles which serve as a nucleus for the coke formed during the cracking operation. The feed is also preferably diluted with light liquid hydrocarbon oil such as naphtha or kerosene.

The effluent from this mild thermal cracking or heat-soaking treatment is passed to a settling zone where it is separated into a supernatant clarified oil layer substantially free of solids and suitable for use as a catalytic cracking feed stock and into a bottom layer consisting of a slurry of solids in oil. Separation by settling in this manner is considerably enhanced by the presence of substantial proportions of light distillate oils, particularly of the naphtha boiling range which are preferably added to the oil feed of the thermal cracking or heat-soaking stage.

The clarified oil is fed directly and without further fractionation to a catalytic cracking unit. The bottom slurry is subjected to a coking treatment to convert it into vaporized products and coke. This is preferably done by contacting the slurry at coking conditions with a dense turbulent mass of subdivided solids fluidized by an upwardly flowing gasiform medium to resemble a boiling liquid with respect to appearance as well as hydrodynamic and hydrostatic properties. At least a portion of the fluidized solids may be supplied in the form of solids contained in the oil slurry recovered from the first stage of the process. Seed solids for this first stage may be recovered from the slurry and/or the fluid coking stage.

The entire vaporized product from the coking stage or any portion thereof may be combined with the clarified oil stream for further conversion in the catalytic cracking stage or may be separately fractionated to recover products therefrom. In the first case, it is desirable to maintain the fluid coking stage at conditions of relatively low coking severity, for example at temperatures of about 800°–950° F., so that the vaporizable portion of the feed to this stage may be merely vaporized therein without substantial thermal conversion. This vaporization is substantially aided by introduction of gaseous media such as steam into the fluid coking stage.

Several advantages result from this invention. In the first place, no distillation equipment is required to effect the separation of a stream suitable for catalytic cracking from the effluent of the liquid phase thermal treatment. Since only a relatively small portion of this effluent is subjected to coking, the coking vessel used may be relatively small. Conditions in the coking stage may be readily controlled so as to obtain a variety of products depending on market demands without affecting the basic output of high octane gasoline produced by the process. Depending on temperature and coking severity, substantial proportions of heating oils or chemicals in the form of olefins and aromatics, and/or marketable coke may be recovered in addition to the high octane gasoline. Fluid-type operation of the coking treatment is of particular advantage because the thickened slurry recovered from the settling stage contains coke of suitable shape and size for fluidization.

The process of the invention is applicable to all types of crude distillation residues and other hydrocarbonaceous residues of similar character as well as to whole crudes. The first stage of the process may be any liquid phase heat-soaking treatment adapted to produce substantial proportions of gas oil range hydrocarbon fractions from the heavy oil feed. Conditions suitable for this purpose include temperatures of about 750°–1000° F., pressures of about atmospheric to 3000 p. s. i. g. or higher, and residence times varying from a few seconds to one or two hours or more, all properly correlated to obtain the desired degree of thermal cracking. Ex-

ternally heated coils or pipes, alone or in combination with an expanded soaking zone, may serve as the liquid-phase reaction zone. In accordance with the preferred embodiment of the invention, the first process stage involves dilution of the heavy oil feed with about 20-120 vol. per cent of naphtha and thermal treatment of the diluted feed at temperatures of about 750°-900° F., pressures of about 1000-3000 p. s. i. g., and residence times of about 2-150 minutes in the presence of about 15-100 lbs. of added finely divided coke per bbl. of total oil feed, in a system comprising a heating coil followed by an agitated soaking zone.

The total product of the first stage is cooled sufficiently (for example to 700° F. or lower) to substantially arrest further conversion so that coke will not be formed on subsequent equipment walls. The cooled product is then passed to a settling zone wherein the effluent separates into a bottom slurry layer containing solids and a supernatant oil layer substantially free of solids. The pressure maintained on the settling zone is preferably substantially the same as that in the thermal cracking zone. If the pressure in the settling zone is greatly reduced, it is necessary to provide more intensive cooling than that just indicated to prevent excessive vaporization prior to the entry of the slurry into the settling zone. The vaporization of a substantial portion of the feed will result in an increased viscosity of the slurry and thus lower settling rate.

As an alternative, the feed may be diluted with a relatively large volume of naphtha such as from 2-10 volumes of low boiling hydrocarbons such as naphtha, per volume of residual oil, and the pressure released between the cracking and settling zones. In this case, the vaporization of the excess naphtha resulting from the pressure reduction can be used for cooling the effluent without undesirably increasing the viscosity of the effluent.

The settling zone may comprise a tank or a series of tanks having sufficient volume to provide the required residence time for settling. Quiescence may be provided by suitable baffles designed to prevent internal circulation of the liquid. For example, conventional slurry thickening devices, particularly the type known as "Dorr Thickener" and described in such texts as Riegel Industrial Chemistry, 1937, 3rd edition, page 708, may be readily adapted for these purposes. In devices of this type, the slurry is thickened by settling it, running off part of the liquid and running off to a subsequent thickening stage a slurry richer in solids than the original one. Means may be provided for the continuous discharge of the thickened slurry, overflow of the clarified oil and continuous feed of the slurry produced in the thermal cracking stage. The thickener may comprise a tank with a bottom sloping toward the center and a plurality of plows, rotating slowly so as to drive the thickened mud toward the point of discharge, clarified oil overflowing from points near the periphery and top of the settler while slurry is charged to the center of this uppermost layer, all in a manner known per se.

When using a naphtha-diluted residuum feed to the thermal cracking stage in accordance with the invention the clarified oil may amount to about 13-34 gal. per barrel of total oil feed (residuum + naphtha) and may comprise hydrocarbons varying in molecular weight from the normally gaseous hydrocarbons, such as methane and ethane, to unconverted portions of the original residuum feed which may have normal boiling points above 1100° F. This clarified oil is passed directly to a catalytic cracking system of conventional design, preferably employing the well known fluid catalyst technique, to be converted therein to high octane gasoline.

The thickened slurry containing substantially all the coke added to and formed in the first coking stage and oil amounting to about 7-27 gal. per barrel of total oil feed is passed to a fluid-type coking vessel wherein it is subjected to coking conditions preferably in the

presence of a dense, turbulent, fluidized mass of subdivided coke. Depending on the products desired, the temperature in this fluid coking stage may range from about 800° to about 1400° F. or higher. Temperatures below about 1000° F. are conducive to the formation predominantly of heating oils and catalytic cracking feed stock of the gas oil range; while temperatures of about 1000° to 1200° F. permit the production of increased yields of gasoline, and higher temperatures the formation of gasoline range aromatics and olefins as well as olefinic gases which are useful as chemicals. The heat required for fluid coking may be supplied in any conventional manner, for example by indirect heating of the fluid coke bed or by circulating coke between the coking zone and a suitable coke reheating zone.

A portion of the slurry recovered from the settling stage may be recycled to the first liquid phase heat-soaking stage to supply seed coke required therein, if desired after milling to reestablish a suitable solids particle size of about 5-250 microns diameter. If the particle size of the coke in the thickened slurry is too great for efficient fluidization, say substantially greater than about 200 microns, the thickened slurry as a whole may be subjected to milling prior to the fluid coking stage. Also, coke recovered from the coking stage may be used as seed coke in the liquid phase heat-soaking stage.

Having set forth its objects and general nature, the invention will be best understood from the following more detailed description wherein reference will be made to the drawing.

Referring now to the drawing, the system illustrated therein essentially comprises a liquid phase thermal cracking stage composed of heating coil 11 and soaker 17, a slurry thickener 25, a catalytic cracking stage 31 and a fluid coker 59. The functions and coaction of these elements will be explained hereinafter using the upgrading of a crude distillation residue as an example. It should be understood, however, that the system may be applied to the conversion of other heavy hydrocarbonaceous materials in a substantially analogous manner.

In operation, a crude residuum may be supplied from line 1 by pump 3 to line 5 at a pressure of about 1000-3000 p. s. i. g. Fresh seed coke having a particle size range between about 5 and 250 microns may be fed to line 5 from slurry tank 7. The slurry in tank 7 may be made by mixing coke with fresh feed, naphtha, or kerosene made in the process or obtained from an extraneous source, product bottoms, or combinations of these materials as hereinafter described. The major portion of seed coke should have particle sizes within the range of from 5-250 microns although it may contain a small portion of particles above and below this range. The amount of seed coke used is preferably between 15 and 100 pounds per barrel of total liquid supplied to the thermal cracking step, depending upon the coke-forming characteristics of the feed, the severity of cracking and other variables, but should be sufficient to prevent the building up of coke deposits on the thermal cracking equipment later described. The oil feed in line 5 should contain about 20-120 vol. per cent of light distillate diluent, based on crude residuum.

The resulting slurry is passed through a fired coil 11 located in a furnace 13, wherein it is heated to a temperature of about 800°-850° F. while maintained at a pressure of about 1000-3000 p. s. i. g. Coil 11 is preferably designed for a feed flow velocity sufficient to prevent the seed coke from settling on the coil walls. This velocity may be of the order of from 4-10 ft. or more per second. The effluent of coil 11 is passed substantially at the temperature and pressure of coil 11 via line 15 to soaker 17 wherein it is maintained substantially at the same conditions in a highly turbulent state for a time sufficient to convert about 50-90% of the heavy oil feed into lower boiling vaporizable products and coke. Turbu-

lence may be created in any suitable way, e. g. by means of a stirrer 19. The total residence times of the feed at temperature above 800° F. in coil 11 and soaker 17 may vary between about 5 minutes to 2 hours or more.

As a typical example, the soaker effluent may contain (in addition to added naphtha) the following products, based on the residuum feed to coil 11: about 5–20 vol. per cent of gasoline hydrocarbons boiling up to 450° F., about 25–60 vol. per cent of gas oil boiling in the range of 450°–1050° F. suitable as a catalytic cracking feed, and about 5–60 vol. per cent of unconverted residuum boiling above about 1050° F. The exact proportions of the products will depend both upon the severity of the coking operation and upon the nature of the residuum feed, as will be appreciated by those skilled in the art.

Products are removed from soaker 17 via line 21 and, after cooling below active cracking temperature, are passed to slurry thickener 25. This settler is preferably maintained at substantially the same pressure as the soaker but may be at a lower pressure as previously described. As shown in the drawing, the slurry in line 21 is cooled below cracking temperature, say below 700° F., by admixture with cooled clarified oil from line 22 to prevent further cracking of the oil in the settler. Slurry thickener 25, which may be of the "Dorr Thickener" type described above, should be of sufficient volume and so operated that a residence time is provided adequate to permit the separation of a clarified oil substantially free of suspended coke as an upper layer. By diluting the residuum feed with naphtha as already described and maintaining a temperature in the settling zone only slightly below coking temperatures, for example 500°–700° F., the viscosity of the oil in slurry thickener 25 is low and more rapid settling rates are obtained. A stream of clarified oil is withdrawn from the upper layer through line 27. A portion of the clarified oil is recycled through line 28, cooler 30 and line 22 to the settler 25 to maintain the temperature in the settler below active cracking temperature as already described. The remainder continues through line 27, having a pressure release valve 29 to a catalytic cracking zone 31.

The clarified oil may be catalytically cracked in any desired manner. However, as previously pointed out fluid catalytic cracking is preferred. While the design and operation of such fluid catalytic cracking systems are widely known in the art, it is noted for the sake of completeness that they involve the use of finely divided catalysts, such as various activated clays or composites of silica gel with alumina, magnesia and/or boria, having a particle size range of from about 1–150 microns. The catalyst is maintained in separate cracking and regenerating vessels in a dense, turbulent, fluidized state by gaseous media passing upwardly through the beds at linear superficial velocities of about 0.3–5 ft. per second. The catalyst circulates continuously between the reactor and regenerator, heat for cracking being generated by burning carbon from the catalyst in the regenerator. Conventional conditions include cracking temperatures of about 800°–1000° F., regenerator temperatures of about 950°–1200° F., pressures of from atmospheric to 50 p. s. i. g., the other conditions such as ratio of the amount of catalyst to oil, and space velocity being such as to crack from about 40–80% of the feed boiling above gasoline into other products.

The cracked products are passed from cracking stage 31 via line 33 to product fractionator 35. Normally gaseous hydrocarbons may be recovered via line 37, light naphtha boiling up to about 250° F. via line 39, heavy naphtha having a boiling range of about 250°–450° F. through line 41 and heating oil boiling between about 450° and 650° F. through line 43. The initial condensate may be withdrawn from the bottom of the fractionator and recycled to cracking stage 31 or further treated as will appear hereinafter. A portion of the light or heavy naphtha products

withdrawn from the product fractionator may be passed via branch lines 49 and/or 51 and lines 53 and 9 to serve as feed diluent in the amounts and for the purpose described above.

Returning now to slurry thickener 25, a stream of thickened slurry containing substantially all the coke is withdrawn from the bottom layer in the thickener via line 55 provided with pressure release valve 57. A portion of the slurry in line 55 may be returned by way of line 9 and pump 61 to the slurry tank 7 and mixed with fresh feed to provide seed coke required in coil 11 and soaker 17. The remaining portion of the slurry from line 55 is passed to a fluid coker 59. If the particle size of the coke has grown beyond that desirable for proper fluidization and/or seeding purposes, all or any suitable portion of the slurry in line 55 may be by-passed via line 63 to a disintegrating device 65, such as a conventional ball mill, rod mill, or the like, wherein the coke particles are ground to a suitable size before returning for admixture with fresh feed or to the fluid coker 59.

Coker 59 contains a mass M of subdivided coke having a fluidizable average particle size of about 50–100 mesh. Mass M is maintained in coker 59 at about atmospheric pressure in the form of a dense, highly turbulent, fluidized solids bed having an upper interface L by a fluidizing gas, such as steam, hydrocarbon gases or vapors, etc., introduced through line 71 and suitable gas distributing means, such as grid 73, in amounts sufficient to establish a linear superficial gas velocity within reactor 59, which will maintain a dense highly turbulent bed of solids therein. The temperature of mass M may be maintained at about 800°–1400° F., depending on the products desired, in any manner known per se. For example, a heating coil 75 may be embedded in mass M for this purpose. Instead of an indirect heat supply in this or any similar manner, coke may be withdrawn through a conventional standpipe 77, aerated and/or stripped by gas injected via taps *t*, suspended in air and passed to a combustion zone (not shown) to be heated therein to a temperature about 50°–200° F. above coking temperature and then returned via line 79 to mass M. Systems of this type are well known in the art of reduced crude coking as demonstrated by such patents as U. S. 2,436,160; U. S. 2,485,315 and others. Lines 77 and 79 may also serve, respectively, for the recovery of product coke and the supply of make-up solids. If desired, a portion of the coke withdrawn through line 77 may be transferred to the slurry tank 7 to serve as seed coke for the fresh feed as earlier described.

The amount and temperature of the fluidized solids in the coke 59 should be sufficient to rapidly vaporize the liquid oil introduced through line 55 to prevent the accumulation of any substantial amount of liquid in the coker which would destroy the fluid properties of the bed. In some cases, the amount of vapors formed from the oil may be sufficient to maintain the fluid bed in the coker 59 without the addition of extraneous gas through line 71. The liquid slurry may be injected into the fluid coker below the grid 73.

Vaporous coking products are removed overhead from mass M and may be withdrawn from coker 59 through suitable gas-solids separation means, such as cyclone separator 83 and line 85 and then passed to conventional product recovery equipment (not shown). Solids fines separated in separator 83 may be returned to mass M via dip-pipe 84.

The system illustrated in the drawing permits of various modifications. For example, the heavy cracked oil in line 45 may be passed via line 87 to coker 59 or a part or all may be returned through lines 89, 55 and 9 to coil 11 to be retreated therein along with fresh feed as described. In cases in which the products recovered via line 85 are similar to those recovered from the cracking stage via line 33, the coker products in line 85 may be wholly or in part supplied via line 91 to fractionator 35 to be

treated therein together with the cracking stage effluent as described above. A further highly desirable modification involves passing at least a portion of the coker products from line 85 via lines 91, 92 and 27 into catalytic cracking stage 31 there to be further converted into gas, gasoline, heating oil and coke. In cases where the products from the coker 59 are separately fractionated by equipment (not shown) the light or heavy naphtha separated from these products may be used as a diluent for fresh feed passing to coil 11 in place of, or in addition to, catalytic naphtha fractions from the product fractionator 35. As a further alternative, naphtha or kerosene from an extraneous source may be used as a diluent for the fresh feed rather than that produced by the process. Other modifications within the spirit of the invention may appear to those skilled in the art.

The above description and exemplary operations have served to illustrate specific embodiments of the invention but are not intended to be limiting in scope.

What is claimed is:

1. The process of converting high boiling hydrocarbons into lower boiling hydrocarbons, which comprises feeding a mixture of a heavy hydrocarbonaceous residue with a substantial proportion of naphtha and finely divided solids to a heat-treating zone, subjecting said mixture in said zone to conditions of temperature, pressure and residence time conducive to the production of lower boiling hydrocarbons and coke from said residue substantially in the liquid phase, withdrawing from said zone a slurry of coke-carrying finely divided solids in liquid product, thickening said slurry by a settling treatment to form a clarified oil layer substantially free of solids and a thickened slurry containing said finely divided solids, subjecting at least a portion of said clarified oil layer directly to catalytic cracking in a catalytic cracking zone and treating at least a portion of said thickened slurry in the presence of a dense, turbulent, fluidized bed composed of subdivided coke produced in the process at vapor phase oil coking conditions in a coking zone to produce volatile coking products and coke.

2. The process of claim 1 in which at least a portion of said volatile coking products is passed to said catalytic cracking zone.

3. The process of converting high boiling hydrocarbons into lower boiling hydrocarbons, which comprises adding finely divided coke to a feed oil rich in constituents boiling substantially above the gas oil range, said feed oil containing substantial proportions of a naphtha diluent, feeding the mixture obtained to a heat-treating zone, subjecting said mixture in said zone in a turbulent state to conditions of temperature, pressure and residence time conducive to the production of lower boiling hydrocarbons and coke from said constituents, substantially in the liquid phase, withdrawing from said zone a slurry of finely divided coke in liquid product, a subjecting said slurry to a settling treatment in a settling zone to form a clarified oil layer and a thickened slurry containing said finely divided coke, subjecting at least a portion of said clarified oil layer directly to catalytic cracking in a catalytic cracking zone, separating the effluent of said cracking zone into several fractions including a naphtha fraction and heavy bottoms, returning a portion of said naphtha fraction to said mixture, and subjecting at least a portion of said thickened slurry to vapor phase oil-coking conditions in a coking zone while maintaining said finely divided coke of said slurry in said coking zone in the form of a dense, turbulent, fluidized mass of solids, to produce volatile coking products and coke.

4. The process of claim 3 in which a portion of said thickened slurry containing finely divided coke is returned to said mixture.

5. The process of claim 3 in which said settling treatment is carried out at a temperature substantially below said heat-treating temperature and substantially at said heat-treating pressure.

6. In the process of converting heavy hydrocarbonaceous residues of the type of reduced crudes into lower boiling hydrocarbons by diluting said residues with a light distillate oil, subjecting the diluted residues in the presence of added finely divided coke in a highly turbulent state to liquid phase thermal cracking conditions to produce said lower boiling hydrocarbons and coke in a thermal treating zone, and recovering said lower boiling hydrocarbons from said treating zone, the improvement which comprises withdrawing a slurry of finely divided coke in liquid coking products from said zone, subjecting said slurry to a settling treatment to form a clarified oil layer substantially free of coke and a thickened slurry containing said finely divided coke-carrying solids, subjecting said clarified oil layer directly to catalytic cracking in a catalytic cracking zone and subjecting at least a portion of said thickened slurry to oil coking conditions in a coking zone while maintaining said finely divided coke of said slurry in said coking zone in the form of a dense, turbulent, fluidized mass of solids.

7. The process of claim 6 in which said oil coking conditions comprise substantially atmospheric pressure and temperatures of about 800°–950° F., steam being added to said coking zone.

8. The process of claim 7 in which volatile products produced in said coking zone are passed to said catalytic cracking zone.

9. The process of claim 6 in which said finely divided coke comprise coke produced in said coking zone.

10. The process of claim 6 in which said distillate oil comprises naphtha boiling in the range of 250°–450° F. produced in said catalytic cracking zone.

11. A process according to claim 1 wherein the mixture in said heat-treating zone is maintained at a temperature between about 750° F. and 1000° F., at a pressure between about atmospheric and 3000 lbs. per square inch for a time between about a few seconds to 150 minutes.

12. The process of claim 5 in which said naphtha diluent has a boiling range of 250°–450° F. and amounts to 50–100 volume percent of said feed, said finely divided coke having a particle size of under 250 microns, being composed of at least a portion of the coke in the said thickening slurry and being added in amounts of 50–100 pounds per barrel of feed, and said conditions in the heat treating zone including a temperature range of about 750°–850° F., pressure of about 1000–3000 p. s. i. g., and residence time of about 2–180 minutes.

References Cited in the file of this patent

UNITED STATES PATENTS

2,073,456	Sachs	Mar. 9, 1937
2,101,641	Cooke et al.	Dec. 7, 1937
2,271,096	Ruthruff et al.	Jan. 27, 1942
2,294,584	Thomas	Sept. 1, 1942
2,379,471	Barron	July 3, 1945
2,403,486	Barron	July 9, 1946
2,453,641	Reed	Nov. 9, 1948
2,557,748	Liedholm	June 19, 1951