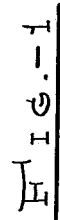


**2,717,865**

3 Sheets-Sheet 1



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Sept. 13, 1955

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2,717,865

COKING OF HEAVY HYDROCARBONACEOUS RESIDUES

Filed May 17, 1951

3 Sheets-Sheet 2

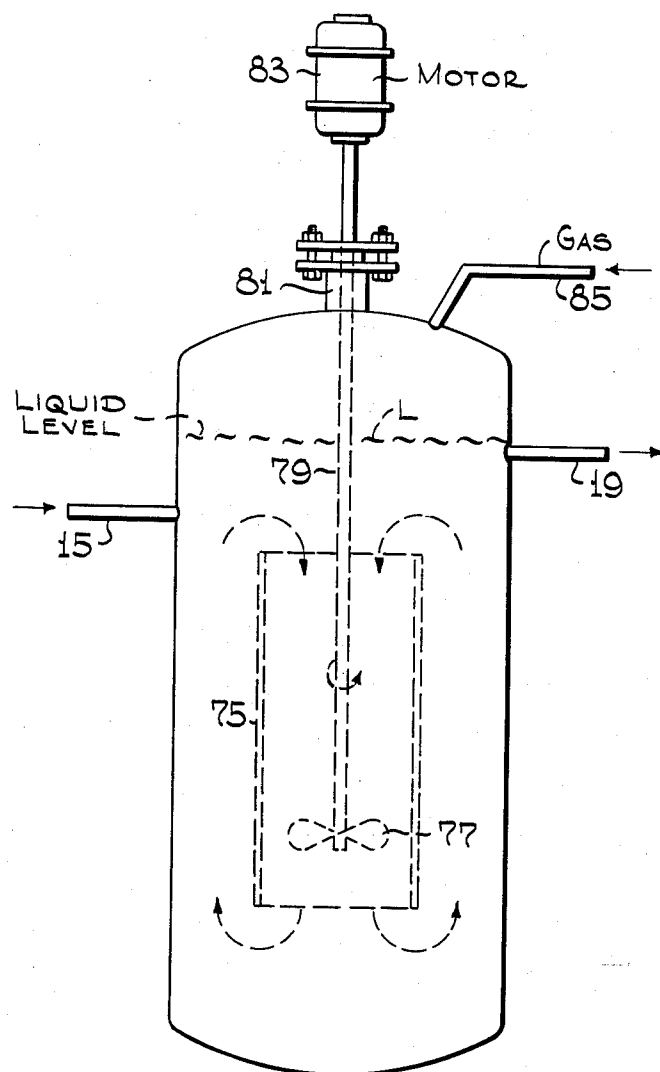


FIG.-2

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3 Sheets-Sheet 3

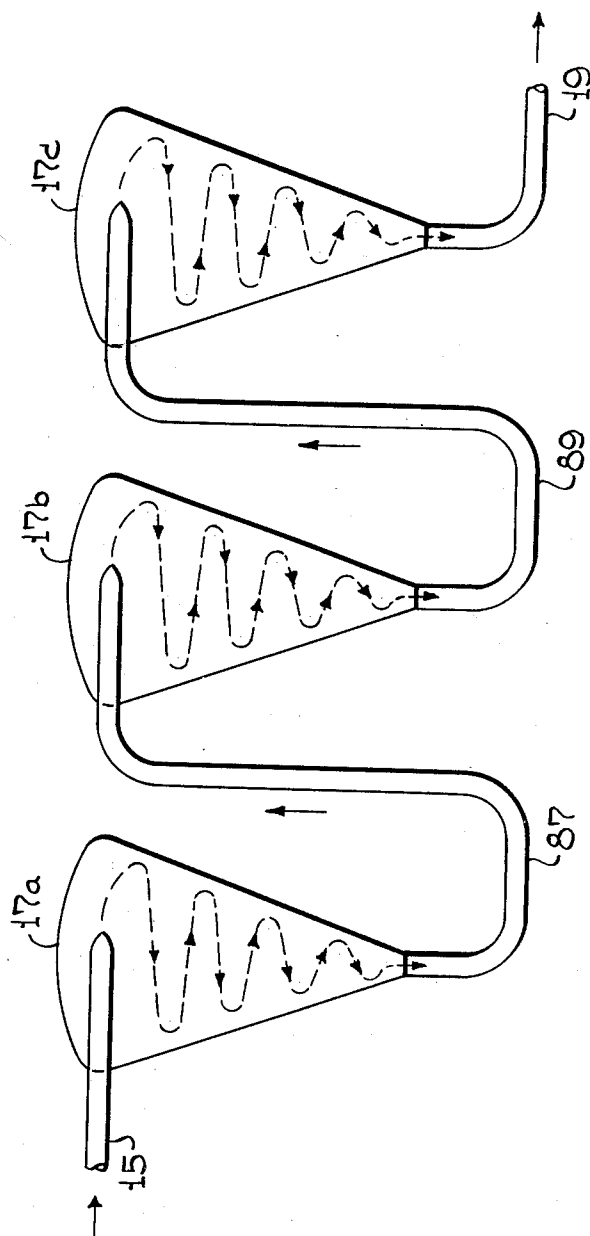


Fig. 3

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2,717,865

## COKING OF HEAVY HYDROCARBONACEOUS RESIDUES

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Application May 17, 1951, Serial No. 226,893

10 Claims. (Cl. 196—55)

The present invention relates to a method of treating hydrocarbons. More particularly the invention pertains to an improved process of coking heavy hydrocarbonaceous residues such as topped or reduced crudes, pitches, asphalts or the like to produce lower boiling more valuable materials, including gasoline, heating oils and gas oils under sufficient pressure to maintain a liquid phase. The improvement of the invention resides in diluting the heavy residual oil feed with a light distillate oil of the naphtha boiling range and coking the diluted feed in the presence of subdivided solids while maintaining turbulence in the liquid phase undergoing coking.

In the past, heavy residual oils particularly the residues from atmospheric or vacuum crude distillation have been coked in intermittent processes wherein the feed stock is heated to coking temperatures and discharged in liquid phase into a heat insulated soaking drum to remain therein at coking conditions for a sufficient length of time to effect the desired conversion into lower boiling products. In the course of this heat treatment large quantities of hard adherent coke are formed which is deposited on the walls of the heating coils and soaking drum. At frequent intervals the process must be interrupted to remove coke deposits and thus to prevent plugging and overheating of the equipment.

Various proposals have been made to cope with coke formation in a manner permitting continuous operation of the coking process. For example, stirring and scraping means of many types have been suggested for incorporation into the soaking drum to keep the coke from adhering to the drum walls and to produce the coke in the form of a loose particulate mass which may be continuously removed from the bottom of the drum. Aside from the fact that the irregular size and shape of the coke so produced greatly complicate its smooth continuous removal, methods of this type fail to prevent coke deposition in the heating coils where the danger of overheating and hazardous pipe failure is particularly great. More successful methods are those in which a finely divided solid such as sawdust, coke, sand, or the like is added to the oil feed with the result that the coke formed is deposited on the added solids to form coked particles of relatively uniform size and shape which may be more readily removed in continuous operation and which simultaneously serve as a scouring agent to remove loosely adhering coke deposits from the equipment walls. However, neither this expedient alone nor in combination with stirring means of the type previously suggested completely eliminates reactor fouling by coke deposition. The present invention overcomes this difficulty.

It is therefore the principal object of the present invention to provide improved means for preventing coke deposition on the reactor walls in systems for the liquid phase coking of heavy hydrocarbonaceous residues. 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 in which:

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Fig. 1 is a semi-diagrammatical illustration of a system adapted to carry out a preferred embodiment of the invention; and

Figs. 2 and 3 are similar illustrations, on a larger scale, of soaker designs suitable to carry out preferred modifications of the invention.

It has now been found that reactor fouling by coke deposition on the reactor walls in the liquid phase coking of heavy oils of the type specified may be completely avoided by diluting the feed stock with a light distillate of the naphtha boiling range, carrying out the coking reaction in the presence of added subdivided seed solids and maintaining the reactants in a state of high turbulence during the coking reaction. The diluent and seed solids are added to the heavy oil feed prior to the heating of the latter to coking temperatures. The added diluent decreases the viscosity of the reaction mixture and thus substantially increases the scouring effect of the solids and the slurring effect of turbulence. In addition when the naphtha diluent is present the coke tends to separate as a hard, non-tacky, granular precipitate which does not stick to the vessel walls; in the absence of the diluent the coke first separates as an adhering, gummy precipitate which sticks to the walls and is then finally converted to hard coke.

The process of the invention is applicable to all types of crude distillation residues as well as to whole crudes. The diluent may be virgin naphtha or a corresponding cut produced in the coking process, having a boiling range of about 100° to 650° F. but preferably about 250° to 450° F. Suitable proportions of diluent may vary from about 20 to 120 vol. percent, preferably about 50–100 vol. percent of the total residual oil feed, i. e. fresh residual oil plus recycle bottoms, if any. The seed solids may be those known in the art such as coke, sand, various clays, silica gel, kieselguhr, sawdust, etc. However, coke, particularly coke produced in the coking process is the preferred solid which may be employed in amounts of about 15 to 100 lbs., preferably about 30 to 60 lbs. per barrel of total fresh and recycle oil feed. The particle size of the seed solids may vary within wide ranges say from about 5–250 microns, the smaller sizes such as 5–50 microns being generally preferred. Turbulence in the reaction mixture undergoing coking may be maintained by various conventional mechanical stirring means, the injection of the feed through draft tubes arranged in the coking zone, or similar means. It is preferred however to create turbulence by tangential injection of the feed into the wide end of a plurality of cone type soaking drums in series and withdrawing the product from the narrow ends of the drums.

Regarding the conditions of the coking reaction, pressures sufficient to maintain a diluent concentration of the order specified above in the liquid reaction medium and to prevent the vaporization of most of the light coking products should be used. Pressures of about 1000–3000 p. s. i. g. preferably about 2000 p. s. i. g. are suitable at the temperatures and conversions most desirable for liquid phase coking. These temperatures may vary between about 750° and about 900° F., and preferably about 800°–850° F., and should be correlated to the residence time of the feed at coking conditions. For example, at coking temperatures up to about 750° F. reaction times of say about 2–4 hours or more may be required for a 90% conversion to products boiling below 1050° F. whereas at temperatures as high as 950° F. or higher a reaction period of 2–10 minutes may be sufficient for the same purpose. At a temperature of 775° F. the residence time may be 1–2 hours, at 800° F. ½–1 hour and at 850° F. 5–20 minutes for the same conversion.

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 Fig. 1 of the drawing, a crude residuum such as a 2.5 to 3.5% South Louisiana residuum having a gravity of about 12° API and a Conradson carbon of about 17% 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 of about 5–100 microns may be fed to line 1 from lock hopper 7 or the like to start up the operation, and at certain intervals, as required. However, in normal operation seed coke is preferably supplied from line 9 in the form of a slurry of ground product coke in heavy recycle bottoms and heavy naphtha from the coking treatment as will appear more clearly hereinafter. Downstream of the junction with line 9 the contents of line 5 may consist of a mixture of about 25 to 75 vol. percent of fresh feed, 5 to 45 vol. percent of product bottoms and 15 to 55 vol. percent of product naphtha, this mixture containing about 15 to 100 lbs. of seed coke of 5–100 microns particle size per barrel. This 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. at a pressure of about 2000 p. s. i. g., more or less. Coil 11 is preferably so designed that the feed attains a velocity of at least 4 ft. per second which may reach as much as 10 ft. per second. In this manner, the liquid flow through coil 11 is maintained highly turbulent. This turbulence in combination with the scouring action of the seed coke and the presence of the naphtha diluent prevent coke deposition on the coil walls even within residence times sufficient to permit substantial coking of the feed in coil 11 itself.

The effluent of coil 11 is passed substantially at the temperature and pressure of coil 11 via line 15 to an upper portion of soaker or soaking system 17 wherein it is maintained in a highly turbulent state substantially at the temperature and pressure of coil 11 for a time sufficient to convert about 50 to 90% of the heavy oil feed into distillate products and coke. As pointed out above the time required for this purpose depends to a large extent on the prevailing temperatures. At the conditions here specified total residence times of the feed at temperatures above 800° F. in coil 11 and soaker 17 may vary between about 5 and 60 minutes. Suitable methods for creating turbulence in soaker 17 will be described herein later on with reference to Figs. 2 and 3.

The coked products contain liquid distillate oils and diluent, some vaporized light products, some gases, unconverted feed and slurried seed coke now having a slightly increased particle size due to coke deposition thereon. This product mixture is withdrawn via line 19 from the bottom of soaker 17 and passed to product fractionator 23 after pressure release to substantially atmospheric pressure in release valve 21. Fractionator 23 is preferably so operated that four distillate fractions are produced as follows. Gas and light naphtha boiling below about 200° F. and amounting to about 4–8 wt. percent dry gas and 4–9 vol. percent light naphtha based on residuum feed, are removed as overhead through line 25. Heavy naphtha having a boiling range of about 200°–420° F. and amounting to about 4 to 10 vol. percent of residuum feed is removed through line 27. This naphtha is net production in addition to the naphtha diluent mixed with the feed. A heating oil fraction boiling between about 430° and 650° F. and amounting to about 14 to 28 vol. percent may be recovered via line 29 and a gas oil boiling above 650° F. and amounting to about 12 to 27 vol. percent of residuum feed may be withdrawn through line 31. Non volatile fractions containing the seed coke and product coke in suspension collect in the bottom of fractionator 23 where they may be stripped of lighter materials by steam injected through line 33. These heavy bottoms are withdrawn through line 35 in amounts of about 10 to 50 vol. percent of the total residuum feed. The yield figures given above apply to a feed conversion

of 50–90% to coke, gas and liquid boiling below 1050° F. The heavy bottoms withdrawn through line 35 are preferably further treated as follows.

About 50 to 70 vol. percent of the bottoms in line 35 are branched off into line 37 and passed to a disintegrating device 39 such as a conventional ball mill, rod mill, or the like wherein the coke particles are ground to the above specified particle size desirable for the feed coke. The slurry now containing fine seed coke is pumped by pump 41 into line 9 at the pressure of line 5 and mixed with product naphtha supplied at the same pressure from line 43 as will appear more clearly hereinafter. The total slurry in line 9 is passed to line 5 and coil 11 as described above.

Returning now to line 35, the remainder of the fractionator bottoms is passed through line 45 to any suitable, preferably continuous filtering device such as a conventional rotary filter 47 cooperating through line 49 and buffer tank 51 with a vacuum pump 53 taking suction from the interior of rotary filter 47. The bottoms slurry in line 45 is passed to the surface of filter 47. Part of the liquid constituents is sucked into the interior of filter 47 leaving a wet filter cake of coke. As the filter rotates the filter cake encounters a spray of heavy product naphtha branched off line 27 through line 55 and spray nozzle 57. The naphtha feed rate through nozzle 57 may be about 0.1 to 1 volume per volume of fresh feed. The liquid bottoms adhering to the filter cake are substantially completely washed out by the naphtha spray and carried therewith into the interior of filter 47 wherefrom the liquid is removed via line 49 into tank 51. Coke free of heavy bottoms is removed from filter 47 by a scraper 59 and may be conveyed in any suitable manner through line 61 to a stripper 63 wherein adhering naphtha may be removed by stripping steam supplied through line 65. Product coke may be recovered through line 67 in amounts of about 10 to 20 wt. percent of total residuum feed.

The mixture of wash naphtha and filtrate bottoms collecting in tank 51 is withdrawn through line 69 and pumped by pump 71 into line 43 to be further treated as described above.

In view of the importance of strong turbulence in soaker 17 methods suitable for this purpose are illustrated in some detail in Figs. 2 and 3.

Referring now to Fig. 2, the method illustrated therein employs a single soaker which may take the place of soaker 17 of Fig. 1 like elements being identified by like reference characters. Soaker 17 is provided in its middle section with a concentric draft tube 75 of smaller diameter and height. A stirring propeller 77 supported by a driving shaft 79 is arranged in the lower portion of draft tube 75. Driving shaft 79 is supported in stuffing box 81 and driven by a motor 83 in a direction which causes propeller 77 to take suction from above and to exert a downward propelling action. The effluent from coil 7 enters soaker 17 through line 15 and is withdrawn through line 19 at rates conducive to maintain in soaker 17 a liquid level L in the upper portion. A compressed gas such as product gas or any other inert gas may be supplied through line 85 to protect the bearing surfaces from the abrasive action of the reaction slurry. Under the influence of the stirring and pumping action of propeller 77 which may have a speed of 10 to 100 R. P. M. the feed is circulated at a high speed downwardly through draft tube 75 and upwardly in the space between draft tube 75 and the walls of soaker 17 while at the same time assuming a rotary motion in the direction of the rotation of propeller 77, at least within draft tube 75, as indicated by the flow arrows. The turbulence so created is in most cases sufficient for the purposes of the invention. In some cases, it may even be sufficient to inject the feed from line 15 at a high velocity, in a downward or upward direction, directly into the upper or lower portion respectively, of draft tube 75, without the pro-

vision of any mechanical stirrer or propeller. However, the frictional forces involved make such a procedure rather inefficient.

A method for creating turbulence of considerably higher efficiency without the requirement of mechanical stirring action or moving parts is illustrated in Fig. 3. In this case, three soaking vessels 17a, 17b and 17c take the place of soaker 17 of Fig. 1. These vessels have the form of inverted cones. The hot feed enters through line 15 and flows through vessels 17a, 17b and 17c in series from top to bottom of each vessel filling the same substantially completely with liquid. The bottom of vessel 17a is connected by line 87 to the top of vessel 17b and the bottom of vessel 17b to the top of vessel 17c by line 89 to permit this flow. Coked products are withdrawn through line 19.

In order to create the desired turbulence in vessels 17a, 17b, and 17c the feed is tangentially injected into the wide end of each vessel at a relatively high velocity of about 4 to 20 ft. per second so that the liquid slurry assumes a highly turbulent rotary motion in a generally downward direction in all vessels. The retarding action of frictional forces is at least balanced and may by proper design and operation of the system be overcompensated by the increasing angular velocity of the liquid on its rotary downward path of steadily decreasing radius. The subdivision of soaker 17 into a plurality of vessels as shown permits higher rotation velocities at relatively low feed rates and feed injection velocities and thus more efficient turbulence. It will be understood, of course, that any one or all of the vessels 17a, 17b and/or 17c may have the form of upright cones receiving the feed in the bottom and discharging from the top. This arrangement may even be preferable in some cases, because having the cones with the small end on top will avoid the collection of gas pockets in the soakers which would have the undesired effect of decreasing the residence time of the liquid in the soakers.

While the systems illustrated by the drawing are tube and tank type arrangements representing the preferred modification of the invention it is noted that in many cases soaker 17 may be completely eliminated, provided the velocity in coil 11 is high enough to maintain high turbulence therein and sufficient residence is allowed in coil 11 to obtain the desired conversion. The heavy product naphtha used as the diluent may be replaced wholly or in part by other hydrocarbon oils of similar boiling range, such as virgin naphtha, catalytically cracked naphtha, etc. Other modifications of the systems illustrated may appear to those skilled in the art without deviating from the spirit of the invention.

The invention will be further illustrated by the following specific example.

#### Example

A 2.5% South Louisiana residuum having a gravity of about 12° API and a Conradson carbon of about 17% was diluted with an equal volume of heavy virgin naphtha (boiling range 300°-400° F.). Coke having a particle size of 100-200 mesh was added to this mixed feed in amounts of about 35 lbs. per bbl. of residuum. The slurry so obtained was treated for 1.6 hours in a stirred autoclave at a maximum pressure of 2000 p. s. i. g. and a temperature of 800° F. The results of the run were as follows:

|                                                                         |      |
|-------------------------------------------------------------------------|------|
| Conversion to coke, gas and liquid boiling below 1050° F., percent..... | 88.9 |
| Net yields:                                                             |      |
| Coke, wt. percent.....                                                  | 18.5 |
| Dry gas, wt. percent.....                                               | 7.7  |
| Light and heavy naphtha, vol. percent.....                              | 16.7 |
| Heating oil, 430°/650° F., vol. percent.....                            | 25.9 |
| Gas oil, 650°/1050° F., vol. percent.....                               | 25.9 |
| Material boiling above 1050°, vol. percent.....                         | 11.1 |

In this operation the coke accumulated in the form of loose, hard particles in the bottom of the autoclave and no coke was deposited on the walls of the autoclave.

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 continuous process of coking heavy hydrocarbonaceous residues, which comprises mixing said residues with about 50-100 vol. percent of naphtha diluent boiling in the range of 100° to 650° F. and about 15-100 lbs. of finely divided coke per barrel of residue and subjecting the mixture formed in a suitable reaction vessel to liquid phase coking conditions conducive to a conversion of about 50-90% of said residues into distillate oils and carbonaceous residue, while maintaining in the vessel sufficient turbulence to prevent coke deposition on the walls of the vessel and to promote deposition of the carbonaceous residue on the finely divided coke.
2. The continuous process of coking heavy hydrocarbonaceous residues, which comprises mixing said residues with about 50-100 volume percent of a naphtha diluent boiling in the range of 100 to 650° F. and about 15-100 pounds of finely divided seed coke per barrel of residue, subjecting the mixture formed in a coking zone to liquid phase coking conditions conducive to a conversion of about 50-90% of said residues into distillate oils and carbonaceous residue, while maintaining in the coking zone sufficient turbulence to prevent coke deposition on the confines of the zone and to promote the deposition of the carbonaceous residue on the finely divided coke, withdrawing a slurry of carbonaceous residue in liquid products from said coking zone, subjecting said slurry to distillation in a distillation zone to produce distillate fractions including a naphtha fraction and a gas oil fraction and heavy coke-containing bottoms, withdrawing said bottoms, returning at least a portion of the coke contained in said bottoms to said hydrocarbonaceous residues to supply at least a portion of said seed coke and adding at least a portion of said naphtha fraction to said residues to supply said naphtha diluent.
3. The continuous process of coking heavy hydrocarbonaceous residues, which comprises mixing said residues with substantial proportions of a naphtha diluent boiling in the range of 100 to 650° F. and finely divided seed coke, passing the mixture formed in turbulent flow through a narrowly confined externally heated extended path at liquid phase coking conditions of temperature and pressure, discharging the total effluent of said path into an expanded soaking zone maintained substantially at said liquid phase coking conditions, maintaining sufficient turbulence in said soaking zone to prevent carbonaceous residue deposition on the confines of said soaking zone, controlling the flow of said mixture through said path and soaking zone so as to provide a residence time of said mixture at said coking conditions conducive to the conversion of about 50-90% of said residues into distillate oils and carbonaceous residue, and withdrawing a slurry of coke in liquid product from said soaking zone.
4. The process of claim 1 in which said naphtha diluent has a boiling range of 250° to 450° F.
5. The process of claim 4 in which said conditions include temperatures of about 800°-850° F., pressures of about 1000-3000 p. s. i. g. and residence times of about 5-60 minutes, and said finely divided coke has a particle size of about 5-250 microns.
6. The process of claim 2 in which said naphtha diluent has a boiling range of 250° to 450° F.
7. The process of claim 6 in which said conditions include temperatures of about 800°-850° F., pressures of about 1000-3000 p. s. i. g. and residence times of about 5-60 minutes, and said finely divided coke has a particle size of about 5-250 microns.
8. The process of claim 3 in which said conditions include temperatures of about 800° to 850° F. and pressures of about 1000-3000 p. s. i. g., said residence time is about

5-60 minutes, said finely divided coke has a particle size of about 5-250 microns and said naphtha diluent has a boiling range of 250 to 450° F.

9. The process of claim 3 in which the said slurry is subjected to distillation in a distillation zone to produce distillate fractions including a naphtha fraction and a gas oil fraction and heavy carbonaceous residue-containing bottoms, withdrawing said bottoms and separating at least a portion of said withdrawn bottoms into carbonaceous residue and liquid.

10. The process of claim 9 in which at least a portion of said separated carbonaceous residue is returned to said hydrocarbonaceous residues to supply at least a portion of said seed coke and at least a portion of said naphtha fraction is returned to said hydrocarbonaceous residues to supply at least a portion of said naphtha diluent.

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