

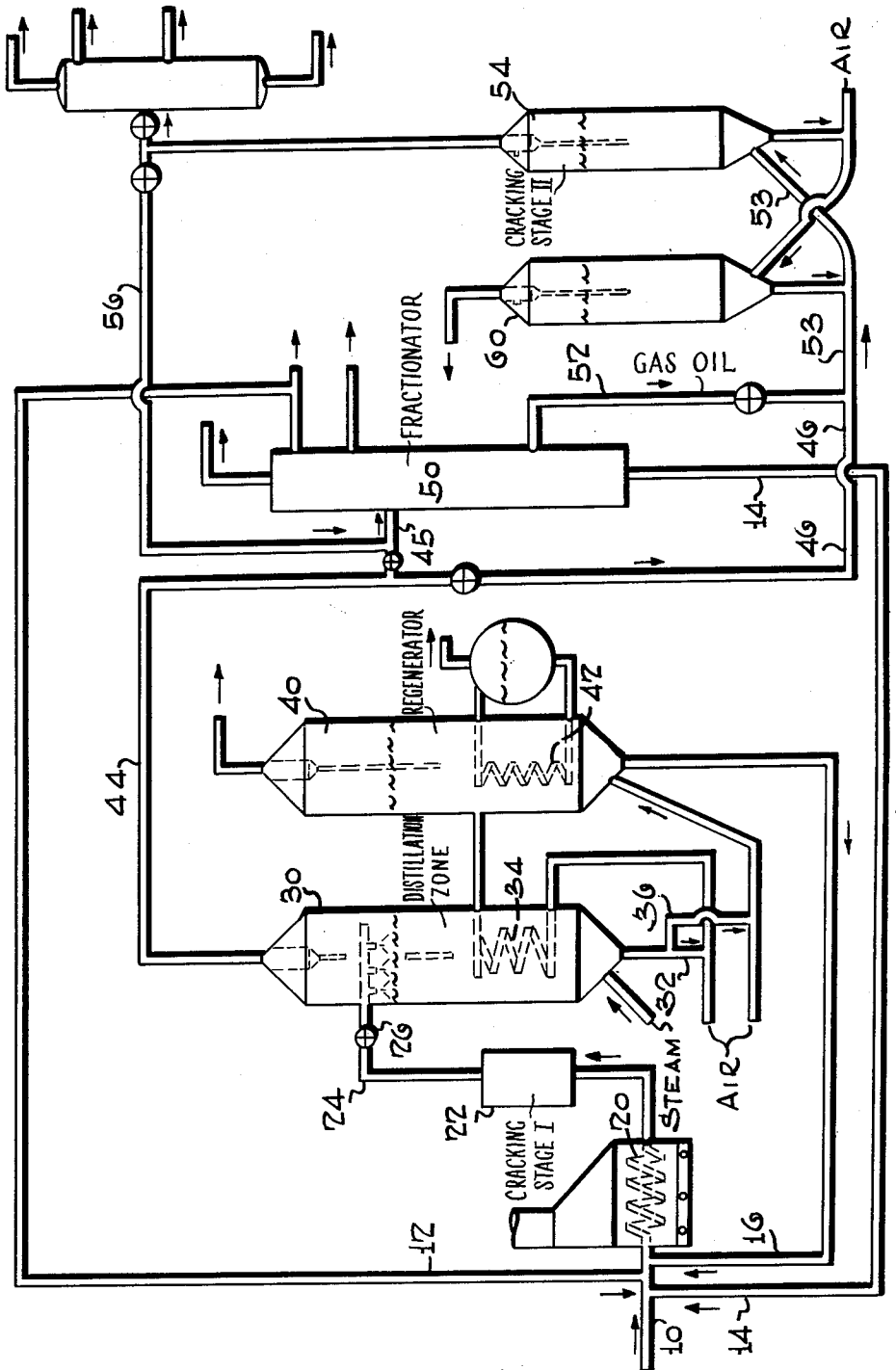
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CATALYTIC CONVERSION OF RESIDUAL OILS

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1

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CATALYTIC CONVERSION OF RESIDUAL OILS

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10 Claims. (Cl. 196—49)

This invention relates to a multi-stage process for catalytically converting heavy hydrocarbon oils into lower boiling products. More particularly, it relates to a process wherein a residual petroleum oil is catalytically cracked in two stages with intermediate distillation in the presence of a dense fluidized bed composed of catalytically inert solids. Still more specifically, in the first stage the feed is catalytically cracked in liquid phase at relatively low temperature and low conversion and the ratio of catalyst to oil is so chosen that the amount of coke produced will completely or almost completely deactivate the catalyst by the time the desired conversion is reached. This coke-deactivated catalyst then behaves like an inert solid and may be used as the fluidized medium in the distillation zone without danger of overcracking.

The present invention is an improvement of a related conversion process previously described in our copending patent application Serial No. 232,523, filed June 20, 1951.

The desire has frequently been expressed for a feasible process for the direct catalytic cracking of petroleum residua or similar heavy hydrocarbon feeds. The chief deterrent to catalytic cracking of residua by conventional means has been the severe catalyst contamination that occurs and that leads to poor product distribution and otherwise reduces the desired effectiveness of the catalyst. Consequently, two-stage vapor phase catalytic processes have been proposed in theory according to which the coke and other contaminants are supposed to be deposited on a catalyst in a first stage intended to minimize the adverse effect of the contaminants, and the resulting "purified" feed is only thereafter subjected to a second catalytic cracking stage wherein the main conversion is supposed to be accomplished. However, the difficulty with this type of operation has been that there was no wholly successful process for carrying out the first catalytic cracking step at sufficiently low conversions, with the result that the feed was principally converted in the first stage under conditions wherein the effectiveness of the catalyst was severely limited, similarly as in a one-stage process. The difficulty lay largely in the fact that in order to achieve the complete vaporization necessary in a vapor phase catalytic cracking process, such as conventional fluid catalytic cracking, high conversion of the residua accompanied by high contamination of catalyst was unavoidable. As a result of this high degree of catalyst contamination, this in turn resulted in undesirably high yields of coke and gas, at the expense of more valuable distillate fractions.

More recent attempts to work out a practical process for converting heavy residua have all but abandoned the idea of direct catalytic cracking. Instead, the trend has been toward first coking the residua in the presence of inert solids and subjecting only the liberated distillate to a catalytic conversion step. Of course, this also has meant considerably poorer product distribution and poorer product quality than in an all-catalytic conversion.

2

Thus, it is the main object of this invention to provide a commercially practical, all-catalytic process for converting heavy hydrocarbons. A more specific object is the devising of a multi-stage process wherein the hydrocarbon feed is catalytically cracked at low conversions in a first stage, the resulting distillate is separated from the first-stage catalyst without appreciable chemical change, and is subsequently cracked in the presence of an active catalyst. These and other objects of the invention, as well as the general nature thereof, will be more clearly understood from the following illustrative example. In this example, the invention is described with reference to the attached drawing which schematically shows one form of apparatus wherein the novel process may be conveniently conducted.

The feeds to the present process preferably comprise vacuum residua which are obtained by the vacuum distillation of crude petroleum oils and may have API gravities in the range of about 0° to 16°, Conradson carbon contents in the range of about 5 to 35 wt. per cent, an initial atmospheric boiling point above about 1000° F., and viscosities above about 200 seconds Saybolt Furol at 210° F. However, other feeds may be employed such as atmospheric residua, whole crude oils, tars and pitches from various refining operations, as well as gas oils, especially the heavy gas oils.

Referring to the drawing, residuum feed having an API gravity of about 7.5°, a Conradson carbon of about 20 weight per cent, and an initial boiling point above 1050° F. at atmospheric pressure, preferably preheated to about 500 to 650° F., is introduced into the system through line 10 wherein it is mixed with a finely divided cracking catalyst or with a mixture of catalyst-containing powdered solids introduced through line 16. The feed is diluted with about an equal volume of naphtha from line 12. In addition, one may also mix the feed with heavier streams recycled within the process such as the distillation bottoms shown in line 14, which may also contain catalyst fines from the second catalytic stage described later.

The purpose of the diluent naphtha is to decrease the viscosity of the residuum. This aids in obtaining high turbulence in subsequent heating and conversion zones and thus tends to prevent fouling of the reaction vessel walls and the deposition of coke thereon. However, the diluent naphtha may be omitted when the feed itself is not unduly viscous, or steam may be used in place of naphtha. The amount of added naphtha may vary from about 0 to 60 gal., preferably 15 to 25 gal., of naphtha per barrel of residuum feed. The amount of recycle oil introduced by line 14 may amount to about 1 to 30 volume percent based on the residuum, for example, but may be entirely omitted. When desired, fines of relatively high grade catalyst may be recovered from the recycle oil before it is mixed with the residuum feed.

Instead of using diluents, or in addition thereto, high turbulence may also be obtained in coil 20 and soaker 22 by suitable design and by other means such as mechanical agitation in soaker 22. Also instead of using a single soaker 22, a plurality of vessels may be used if desired.

The catalyst introduced by line 16 may be any contact cracking catalyst having fluidizable particle size characteristics, that is, a particle size ranging up to about 400 microns, preferably between 20 and 150 microns. Suitable catalysts include acid treated clays, synthetic composites of silica and alumina, silica and magnesia, alumina and boria, aluminum fluoride, and so on. Catalyst that has been previously used in the second cracking stage of the present process or in other fluid processes for the catalytic cracking of gas oils and the like is satisfactory for use in the first cracking stage herein.

The mixture of hydrocarbon feed and catalyst is passed

from line 10 through a first cracking stage constituted by heated coil 20 and soaker 22 where it is maintained under reaction conditions for a sufficient time to achieve the desired conversion. Such reaction conditions in zones 20 and 22 may comprise temperatures between about 700 to 900° F., preferably 750 to 850° F., and pressures sufficient to maintain the major portion of the oil in liquid phase. Depending partly on the amount of added naphtha or similar relatively volatile constituents present, the reaction pressure may range from about 500 to 3000 p. s. i. g., higher concentration of volatile constituents requiring relatively greater pressures for keeping the reaction mixture in liquid phase. The combined residence time in zones 20 and 22 may vary from about 2 to 60 minutes, preferably about 10 to 30 minutes above 650° F.

To achieve the main purposes of the present invention, it is desirable to keep the formation of dry gas (up to and including C₃) in the first cracking stage below about 5 weight percent, preferably between about 1 to 3 weight percent based on residuum feed. This conversion in the presence of catalyst has been found to cause sufficient cracking of the large residuum molecules to convert them into high quality products capable of vaporization in a subsequent non-catalytic distillation zone without further appreciable decomposition. At the same time, such a conversion has been found low enough to keep non-catalytic decomposition of the feed in the first stage at a negligible minimum.

The amount of active catalyst used in the first cracking stage may vary between about 20 to 200 lbs., preferably 50 to 120 lbs. per barrel of residuum feed. Within these limits, the optimum amount of catalyst varies with the type of feed used and with the activity level of the catalytic solids. It is best chosen so as to give at least some catalytic effect during the entire cracking stage, while the catalyst is being covered with non-catalytic contaminants, principally coke. Consequently, a relatively large amount of catalyst is required when a feed having high coke-forming tendencies is being processed and also when the catalyst-containing solids have relatively low catalytic activity, and vice versa. At the same time, it is essential to the purposes of this invention to choose the amount of catalyst so that the amount of coke laid down thereon by the end of the first cracking stage substantially completely deactivates the catalyst. For instance, about 10 to 60 weight percent of coke based on catalyst may be deposited in this stage depending on the initial activity level of the catalytic solids used.

Of course, some of the advantages of the present invention may also be obtained if inert solids such as coke are used in the first stage instead of catalyst, as more particularly described in our aforesaid patent application Serial No. 232,523. However, in such a case, poorer product distribution and quality are obtained, and larger equipment may be necessary to compensate for the larger holding time required if the first stage is non-catalytic.

The converted reaction mixture containing the substantially completely spent or deactivated catalyst is passed from soaker 22 through line 24 and pressure release device 26 and sprayed or flashed into the upper disperse phase of distillation zone 30, where the oil is rapidly vaporized from its burden of spent catalyst. Since the catalyst entering distillation zone 30 through line 24 is substantially deactivated by coke, the mass of fluidized solid formed therefrom in the lower part of zone 30 is also substantially inert and incapable of causing further significant conversion of the oil during the relatively short residence time of the oil in the distillation zone. An inert gas such as steam may be introduced into the bottom portion of distillation zone 30 in amounts ranging from about 1 to 20 weight percent on residuum feed. Such addition of steam is usually desirable both for the purpose of stripping oil vapors from the fluidized solids and to aid in maintaining proper fluidization, since the volatile hydrocarbons vaporized in the distillation are usually insufficient to give velocities high enough for good fluidization. As

is well known, good fluidization usually requires that the total linear superficial gas velocity in the fluidized bed be between about 0.5 and 5 ft./sec., or preferably between 1 and 3 ft./sec.

The pressure in distillation zone 30 may be substantially atmospheric, that is, between about 15 and 50 p. s. i. absolute, although vacuum or moderate pressures may be used. The temperature in the distillation zone may be from about 850 to 1050° F., preferably 900 to 950° F., but not high enough to cause appreciable thermal decomposition of the oil being distilled.

A portion of the coke-bearing catalyst, preferably after stripping, may be withdrawn from distillation zone 30 by line 32 and the coke thereon burned in coil 34 which may be embedded in the dense bed in zone 30 in order to supply the required heat thereto; the outlet of coil 34 may enter regenerator 40 described hereafter. Alternative means of heating distillation zone 30 may be employed also. The remainder of the coke-bearing catalyst is removed from zone 30 by line 36 at a rate sufficient to maintain the upper surface of the dense turbulent bed in zone 30 at a constant level. This removed catalyst is then suspended in an oxygen-containing gas such as air and introduced into a regenerator 40 where substantially all of the coke may be burned off while the catalyst is again maintained as a dense turbulent bed. Regenerated catalyst is finally withdrawn from regenerator 40 and recirculated to line 10 by aforementioned line 16. If a higher solids recirculation rate through line 16 or lower catalytic activity in reactor coil 20 is desired, the catalyst may be only partially regenerated in vessel 40. Also when using a feed of relatively low coke forming tendency, it may be impractical to deposit enough coke on the catalyst to accomplish the high degree of catalyst deactivation desired in the first conversion stage. Consequently, in such a case partial regeneration would be of value, leaving say 3 to 8 weight percent coke on the catalyst being recycled from regenerator 40 to line 10 through line 16. Regeneration temperatures in zone 40 are kept below the deactivation temperature of the catalyst, which deactivation temperature may be between about 1100 and about 1200 or 1250° F. depending on the particular catalyst used. Where necessary or desirable, heat may be recovered from regenerator 40 by means of steam generating coils 42 or by equivalent means.

The oil vaporized in distillation zone 30 may be passed therefrom by lines 44 and 45 to fractionator 50 where it can be separated, for instance, into gas, naphtha, heating oil, gas oil, and oil bottoms containing some entrained catalyst which, as mentioned earlier, may be recycled to line 10 by line 14 if desired. A part of the naphtha may also be recycled to line 10 by line 12 and serve therein as the aforementioned diluent. The remaining naphtha and heating oil fractions may be recovered as products and the gas oil fraction may be passed from fractionator 50 by lines 52 and 53 to a conventional catalyst cracking zone 54. In zone 54 this gas oil can be efficiently cracked over a clean and therefore selective catalyst under otherwise known conditions including fairly high conversions to give about 50 to 75 weight percent of 430° F. end point gasoline based on the gas oil feed. As a result, high yields of good quality gasoline and heating oil are produced in addition to the like fractions catalytically produced in the first conversion stage. Of course, instead of fractionating the first-stage products into the several fractions mentioned, they may all be fed directly to the catalytic cracking zone 54 by lines 44, 46 and 53.

The cracked vapors from cracking zone 54 pass by line 56 into line 45 where they may join the vapors from the first cracking zone and then enter common fractionator 50. However, at other times, it may be preferred to fractionate the first-stage products separately from the second-stage products in order to permit individual recovery of the various fractions. For instance, the naphtha from the second stage may have a different octane rating than that from the first stage. Also, it may be prefer-

able to avoid recycling of the gas oil from the second stage if other uses are available.

The cracking catalyst in zone 54 is of relatively good quality and high activity, and is maintained therein at a low degree of contamination, for instance, up to about 1.0 weight percent of coke on catalyst and a negligible amount of mineral contaminants. Consequently, much higher selectivity to gasoline, and a gasoline of better anti-knock qualities, can usually be obtained in zone 54 than in the first cracking stage. Spent catalyst is withdrawn from conversion zone 54 and regenerated in a separate vessel 60 by combustion with air as otherwise well known. So-called "Fluid" catalytic reactors and regenerators as illustrated in the drawing are preferred, though other conversion systems employing the catalyst in the form of fixed or moving beds may be substituted for zone 54 illustrated in the drawing.

In another exemplary run a vacuum residuum derived from a South Louisiana crude oil and having an API gravity of about 11.9°, a Conradson carbon content of about 17 weight percent, a viscosity of about 400 seconds Saybolt Furol at 210° F., and an initial atmospheric pressure boiling point above about 1050° F. was treated according to the present invention. Specifically, this residuum was diluted with an equal volume of naphtha boiling in the range of about 300° to 400° F. and cracking catalyst having a particle size range of about 40 to 120 microns was added in amounts of about 49 pounds per barrel of mixed feed. The cracking catalyst comprised a synthetic silica alumina composite containing about 13% alumina, and was partially deactivated by previous service for cracking gas oils during which it became contaminated with about 0.5 weight percent of inorganic impurities including iron oxide and its surface area was reduced to about 100 square meters per gram. The mixed feed containing catalyst was introduced into heating coil 20 and soaker 22 where it was heated to about 775° F. at a pressure of about 1200 p. s. i. g. Turbulence was provided in soaker 22 by means of mechanical agitation. The residence time in coil 20 and soaker 22 at temperatures above about 760° F. was about 30 minutes. Under these conditions the residual oil was substantially converted to coke and distillable products without fouling of the vessel walls. The coke deposited upon the catalyst in coil 20 and soaker 22 amounted to about 23 pounds per barrel of mixed feed or about 47 weight percent on catalyst. This amount of coke substantially deactivated the catalyst so that it was incapable of promoting any significant additional amount of cracking during the short residence time of the oil in the subsequent distillation zone 30.

The cracked products containing coke-bearing catalyst were introduced into fluid solids distillation zone 30 containing a fluidized bed of coke-deactivated catalyst maintained at about 950° F. and about 0 p. s. i. g. Steam amounting to about 20 weight percent of the oil feed was introduced into distillation zone 30 to maintain the coke-deactivated catalyst in a fluidized condition and to aid in the distillation process. The oil feed rate to distillation zone 30 was about 5 weight per hour per weight of coke-deactivated catalyst present in zone 30. As the cracked oil was introduced into zone 30 it was rapidly vaporized and removed overhead by line 44 without substantial further conversion in zone 30 while the coke-deactivated catalyst entering zone 30 with the oil feed remained in this zone and became a part of the fluidized mass therein until withdrawn at the bottom. The oil vaporized in zone 30 was fractionated in tower 50 (in the absence of second-stage products) and the following yields of products were recovered for each barrel of mixed naphtha and residuum feed: (1) about 2.5 lbs. of dry gas, (2) about 24.2 gal. of gasoline cut boiling below about 430° F. (including the naphtha introduced in the feed as diluent), (3) about 4.3 gal. of heating oil boiling in the range of about 430° to 650° F., (4) about 9.6 gal. of gas oil boiling in the range of about 650° to 1000° F., and

(5) about 2.1 gal. of higher boiling bottoms suitable for fuel oil or for recycling to the first conversion stage. The isolated gas oil was then catalytically cracked further in "Fluid" zone 54 and an additional volume of valuable gasoline and other products was obtained.

In summary, it is seen from the foregoing description and example that the present invention provides for a conversion just about high enough to permit vaporization of the residuum in the presence of a relatively contaminated catalyst in a first stage, followed by extensive conversion over a relatively non-contaminated, selective catalyst in a second stage. Thus, high over-all selectivities favoring formation of the most desired products are assured. Various modifications not specifically described herein may become apparent to those skilled in the art, without departing from the spirit of the present invention for which patent protection is desired within the full scope of the appended claims.

The claims:

1. In a process for cracking heavy residual oils having a Conradson carbon of about 5 to 35 weight per cent and an atmospheric boiling range substantially above 1000° F., the improvement which comprises mixing the heavy residual oil with 20 to 200 lbs. of finely divided cracking catalyst per barrel of residual oil, passing the mixture through a conversion zone at 700 to 900° F. and at a pressure between 500 to 3000 p. s. i. g. which is sufficient to maintain a major portion of the residual oil in liquid phase, keeping the mixture under the said reaction conditions for a residence time between about 2 to 60 minutes to produce a conversion corresponding to not more than 5 weight per cent of dry gas formation based on residual feed and until the catalyst is just substantially completely deactivated by deposited coke, releasing the pressure on the converted mixture and passing the mixture into a distillation zone containing a dense fluidized bed of inert solids in the lower part thereof whereby the coke-bearing catalyst becomes part of the fluidized bed, maintaining the distillation zone at substantially atmospheric pressure and at a temperature between about 850 to 1050° F. and high enough to vaporize the converted oil without substantial decomposition, removing the converted oil vapors from an overhead portion of the distillation zone and withdrawing solids from the bottom of the distillation zone.

2. A process according to claim 1 wherein the residual oil feed is diluted with 15 to 60 gallons of naphtha per barrel of feed and wherein the temperature in the conversion zone is between 750 and 850° F.

3. A process according to claim 1 wherein the residence time of the reaction mixture in the conversion zone is between 10 and 30 minutes and produces a conversion corresponding to about 1 to 3 weight per cent dry gas formation based on residual oil feed.

4. A process according to claim 1 wherein the catalyst concentration in the reaction mixture is between 50 and 120 pounds per barrel of residuum and results in deposition of about 10 to 60 weight per cent of coke on catalyst at the end of the conversion.

5. A process according to claim 1 wherein an inert fluidizing gas is introduced at the bottom of the distillation zone at a rate sufficient to produce a total superficial gas velocity of about 0.5 to 5 feet per second in the dense fluidized bed.

6. A process according to claim 1 wherein a portion of the coke-bearing catalyst withdrawn from the distillation zone is mixed with an oxygen-containing gas under combustion supporting conditions and the resulting hot mixture is passed in indirect heat exchange relation through the dense fluidized bed of the distillation zone at a rate sufficient to supply the required heat of distillation.

7. A process according to claim 1 wherein a portion of the coke bearing catalyst withdrawn from the distillation zone is mixed with an oxygen-containing gas, the

coke is burned off at 1100 to 1250° F. and below the deactivation temperature of the catalyst, and the resulting regenerated catalyst is recycled for mixing with further amounts of fresh residual oil.

8. A process according to claim 1 wherein the oil vapors removed from the distillation zone are fractionated in a fractionation zone to give a naphtha cut, a gas oil cut and a bottoms cut, and wherein the bottoms cut is mixed with fresh residual oil feed in a proportion of 1 to 30 volume per cent based on the residual oil.

9. A process according to claim 8 wherein the separated gas oil cut is passed under cracking conditions through a second conversion zone containing selective cracking catalyst and wherein the cracked hydrocarbon products from the second conversion zone are mixed with the vaporized oil removed from the distillation zone prior to passing the resulting hydrocarbon mixture jointly to the fractionation zone.

10. In a process for cracking heavy residual oils having a Conradson carbon of about 5 to 35 weight per cent and an atmospheric boiling range substantially above 1000° F., the improvement which comprises mixing the heavy residual oil with 20 to 200 lbs. of finely divided cracking catalyst per barrel of residual oil, passing the mixture through a first conversion zone at 700° to 900° F. and at a pressure between 500 and 3000 p. s. i. g. which is sufficient to maintain a major portion of the residual oil in liquid phase, keeping the mixture under the said reaction conditions for a residence time between about 2 to 60 minutes to produce a conversion corresponding to not more than 5 weight per cent of dry gas fraction based on the residual feed and until the catalyst is just substantially completely deactivated by deposited coke,

releasing the pressure on the converted mixture and passing the mixture into a distillation zone containing a dense, fluidized bed of inert solids in the lower part thereof whereby the coke-bearing catalyst becomes part of the fluidized bed, maintaining the distillation zone at substantially atmospheric pressure and at a temperature between about 850° to 1050° F. and high enough to vaporize the converted oil without substantial decomposition, removing the converted oil vapors from an overhead portion of the distillation zone, withdrawing solids from the bottom of the distillation zone, fractionating the oil vapors to give a naphtha cut, a gas oil cut and a bottoms cut, admixing the bottoms cut with fresh residual oil feed in a proportion of 1 to 30 volume per cent based on the residual oil, cracking the gas oil cut in a second conversion zone with finely divided cracking catalyst, removing spent catalyst overhead from the second conversion zone with cracked hydrocarbon vapors and admixing the spent catalyst with fresh residual oil being fed to the first conversion zone.

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