

July 15, 1958

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2,843,530

RESIDUUM CONVERSION PROCESS

Filed Aug. 20, 1954

2 Sheets-Sheet 1

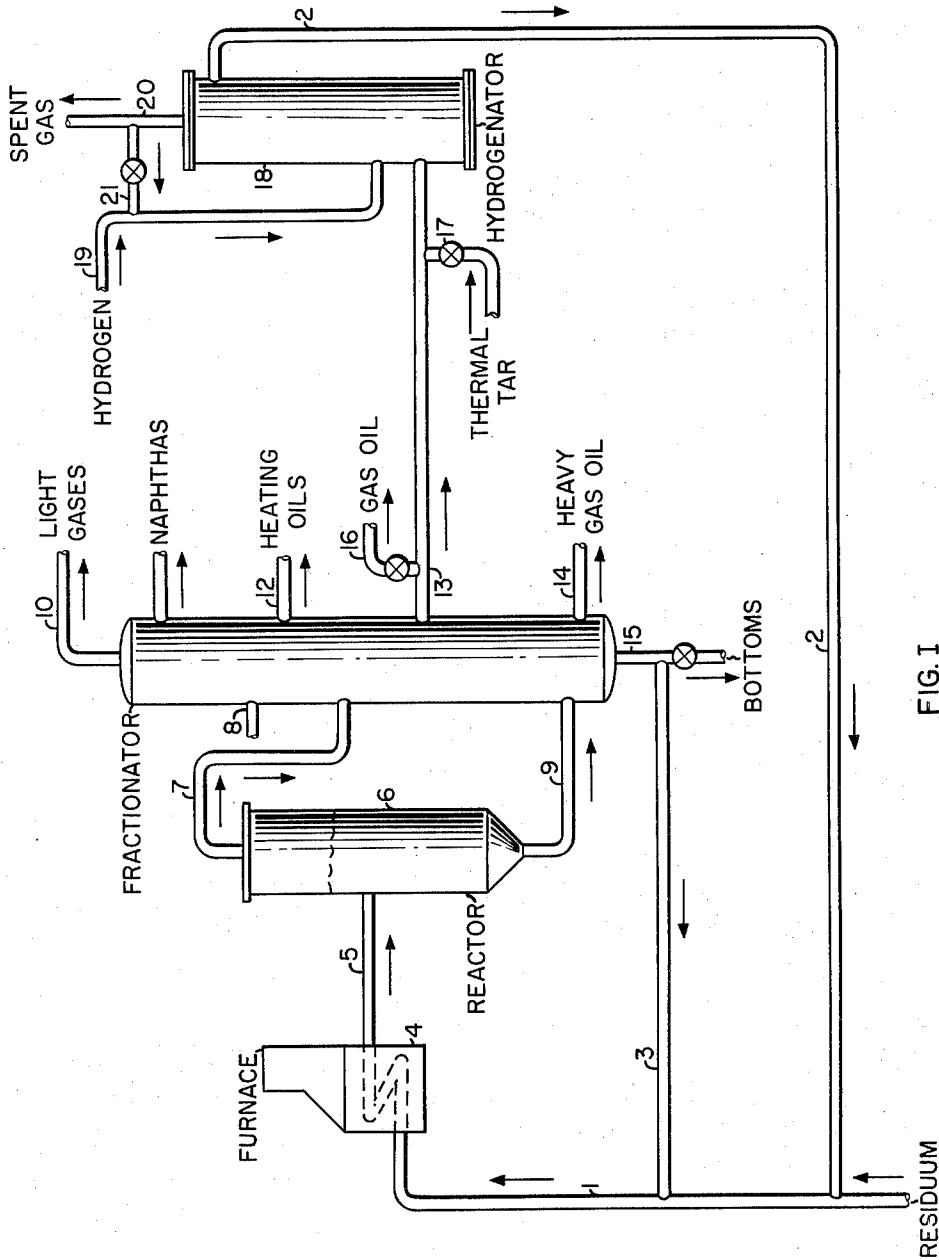


FIG. 1

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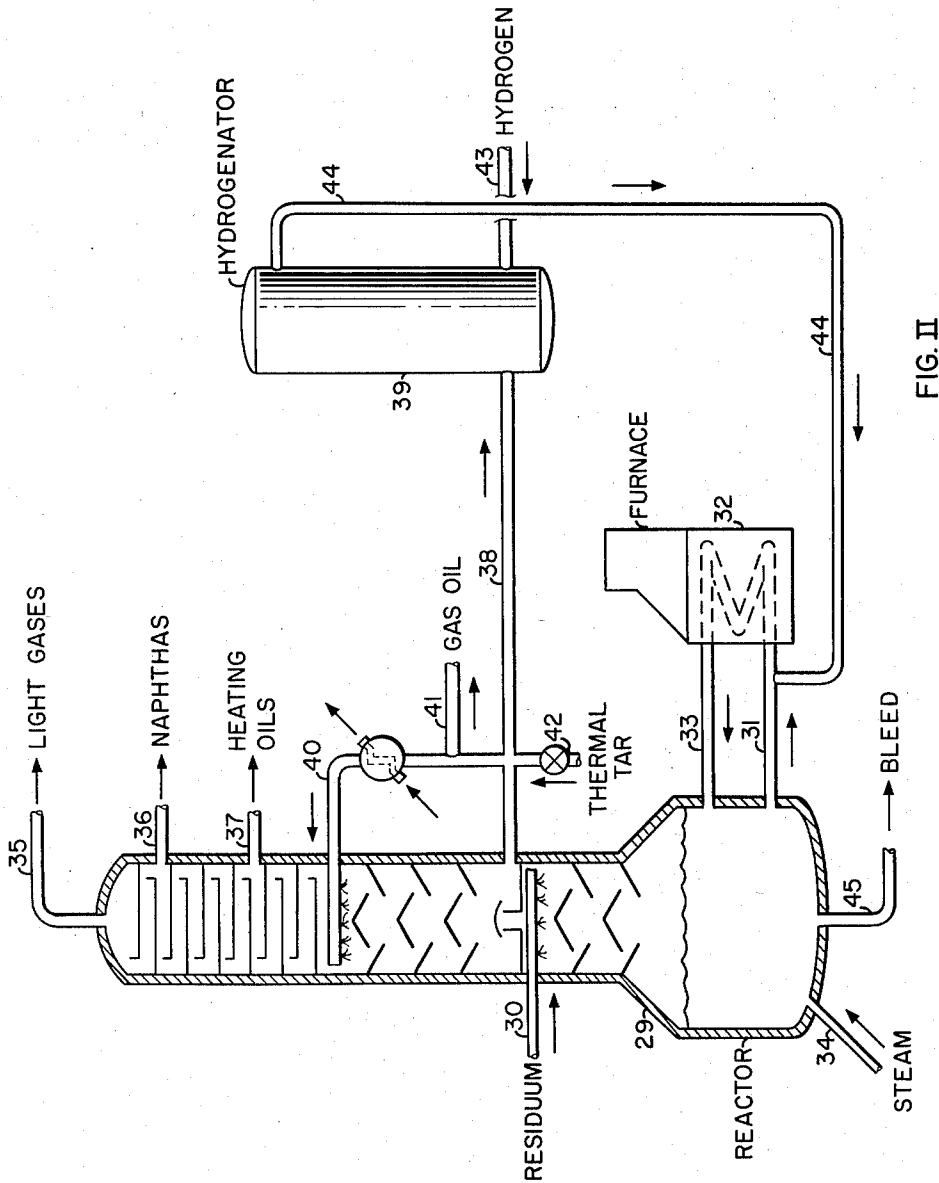


FIG. II

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## RESIDUUM CONVERSION PROCESS

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Application August 20, 1954, Serial No. 451,254

4 Claims. (Cl. 196—50)

This invention pertains to the converting of hydrocarbon oils by hydrogenolysis. More particularly it is concerned with the upgrading of petroleum oils, particularly heavy high boiling oils such as vacuum residua by thermal cracking of the oil in the presence of a hydrogen donor diluent. By the process of this invention, low value hydrogen deficient oils having coke forming propensities during thermal cracking are converted to more volatile products such as light distillates for use as motor fuels and gas oils suitable as feed stocks for catalytic cracking processes.

A process termed hydrogen donor diluent cracking (HDDC) has recently been proposed. In this process, a heavy, low value oil is upgraded by admixing it with a hydrogen donor diluent material, aromatic-naphthenic in nature, and thermally cracking the mixture as in a thermal cracking coil. The hydrogen donor diluent is a polycyclic condensed ring aromatic or an aromatic-naphthenic material that has been especially prepared by partial hydrogenation from selected normally surplusage, refinery streams such as catalytic cycle stocks, thermal tars, etc. The hydrogen donor diluent used has the ability to take up hydrogen in the hydrogenation zone and readily release it to hydrogen deficient oil in a thermal cracking zone. In this manner of hydrocracking oils, the oil being upgraded, usually a residual oil, is not contacted directly with the hydrogenation catalyst and does not, therefore, impair the activity of the catalyst by contamination. The amount of concomitant light gases and coke produced by this process is relatively small, usually being in the order of about 5 to 10%. This technique of HDDC is more fully presented by co-pending and now abandoned application entitled, "Upgrading of Heavy Hydrocarbon Oils," Serial No. 365,335, filed July 1, 1953, by Langer, a co-inventor of the present invention.

In the above-described HDDC process wherein the products, unconverted feed and spent diluent are continuously removed from the reactor as an equilibrium mixture, in order to obtain high conversions, it has been necessary to separate and recycle unconverted materials from the reaction mixture. Further, it has been necessary to use a high hydrogen donor diluent to residuum ratio to prevent coking in the reactor and to secure reasonable conversions. The present invention proposes a novel method of hydrogen donor diluent cracking that overcomes these disadvantages.

According to the present invention, a hydrogen donor diluent is admixed with a hydrogen deficient oil and the resulting mixture is subjected to liquid phase thermal cracking. During the thermal cracking the conversion products are continuously removed overhead as vapors. This practice greatly increases the ratio of hydrogen donor diluent to unconverted material in the liquid phase. Consequently, coke deposition is greatly minimized or eliminated and a much more efficient use is made of the hydrogen donor diluent than has been made in previously pro-

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posed processes. In the previous processes, the spent hydrogen donor diluent and the conversion products, along with unconverted material, have been removed from the reactor as an equilibrium mixture of liquid and gases.

5 The withdrawn materials were then separated to obtain the spent hydrogen donor diluent which was partially hydrogenated and recycled, and the unconverted refractory constituents of the feed, which were also recycled to obtain high conversions. Thus, in the past, maximum  
10 use has not been made of reactor capacity. The hydrogen donor diluent has been used inefficiently because of its low concentration and variations in product selectivities were difficult to obtain.

While the main feature of the present invention is a  
15 continuous vapor phase withdrawal of the conversion products, other subsidiary features and advantages of this invention are to be appreciated. Preferably the spent hydrogen donor diluent is withdrawn from the reactor as a liquid and is preferably separated in a common separation system, e. g., a fractionator, with the conversion  
20 products to obtain the spent diluent for hydrogenation. As an alternative, the spent diluent or a portion thereof may also be removed overhead from the reactor as a vapor. Another alternative is to separate the spent  
25 diluent, when it is withdrawn as a liquid, from the unconverted bottoms in a separate separation system. A third alternative is that when the spent diluent is removed as a vapor from the reactor, rather than separately hydrogenating the diluent, the total overhead along with  
30 the diluent may be partially hydrogenated before separation, thereby regenerating the hydrogen donor diluent.

It is an object of this invention to convert hydrocarbonaceous materials, particularly petroleum residua to lighter and more valuable distillates. Another object is  
35 to propose a hydrogen donor diluent cracking process characterized by continuous vapor phase withdrawal of the conversion products.

These and other objects and advantages will become apparent as this description proceeds and the attached  
40 drawings, forming a part of the specification, are described in detail.

In the drawings,

Figure I diagrammatically depicts a preferred embodiment of this invention adapted to the conversion of a  
45 petroleum residuum.

Figure II portrays the modification of the process of this invention in which the thermal cracking reactor and the product separation system are integral.

Charging stocks for the present invention are preferably  
50 hydrogen deficient petroleum derived oils, such as crude oils, distillate and residual fractions therefrom or mixtures thereof. Particularly preferred charging stocks are heavy residual oils characterized by API gravities of  
55  $-5^{\circ}$  to  $20^{\circ}$ , Conradson carbons of 5 to 50 wt. percent, and initial boiling points above  $850^{\circ}$  to  $1100^{\circ}$  F. This invention is, however, capable of enjoying broader applications. Thus, coal tars, shale oils, tars, asphalts, etc. may also be processed by the present invention. It has also been proposed to utilize the HDDC process to extract  
60 and concurrently convert oils from shales and sands. As will hereinafter appear, the present invention also has utility in processing such hydrocarbonaceous materials.

The sources of the aromatic-naphthenic oil that is partially hydrogenated to secure the hydrogen donor diluent  
65 have previously been described. In particular, it has been found that the thermal tars obtained by the thermal cracking of catalytic cycle stocks yield excellent donor diluents. It has also been found, however, that certain lube oil extracts, extracts of catalytic cycle stocks, heavy cycle  
70 stocks themselves, or bottoms from catalytic cracking can serve as a source of the donor diluent. In any case,

the prime consideration for the selection of a hydrogen donor diluent is that the diluent should be composed of predominate proportions of aromatic-naphthenic molecules or condensed ring structures having the ability to take up hydrogen in a hydrogenation zone and release it in a thermal cracking zone. Such condensed ring structures are relatively refractory and will pass through the thermal cracking zone relatively unaltered. The condensed ring structures are susceptible to being recovered from the reaction mixture and being regenerated by partial hydrogenation. However, while a major proportion of the donor diluent material can be continuously reused, there will normally be some loss of the donor diluent and this loss is made up from extraneous sources.

For convenience the pertinent operating conditions applicable to the following description of Figure I are summarized in Table I, presented hereinafter. With particular reference to Figure I, a charging stock, for example, a vacuum residuum, is blended with a hydrogen donor diluent supplied by line 2 and a small amount of recycled bottoms supplied by line 3. The blend is passed to a furnace 4 by line 1. In the furnace, the blend is heated to a suitable thermal cracking temperature, at a pressure sufficient to maintain substantially liquid phase conditions. The heated material is then passed by line 5 to a reactor 6. Each of the streams can, of course, be heated separately and passed to the reactor, if it be desired.

Conversion products boiling below the initial boiling point of the diluent are removed continuously from the vapor phase of the reactor and sent to a fractionator 8 by line 7. A liquid phase bleed is taken from the bottom of the reactor comprising diluent, products boiling above the initial boiling point of the diluent, and some unconverted refractory constituents of the feed. The liquid phase bleed is introduced into the fractionator 8 by line 9 below the point at which the highest boiling distillate is removed as a side stream. Thus both vapor phase and liquid phase products are separated in a single fractionator.

Light gases are removed from the fractionator by line 10. Naphthas are removed by line 11 and heating oils are removed by line 12. A gas oil which contains substantially all of the spent donor diluent is removed by line 13. Heavy gas oil suitable as a catalytic cracking charging stock can be removed by line 14. The remaining bottoms are removed by line 15, a major portion of which are recycled for further treatment.

Up to about 25% of the spent donor diluent may be bled from the process by line 16. Makeup donor diluent, e. g., thermal tar, is admitted to the process by line 17. This makeup thermal tar is necessary in order to maintain the effectiveness of the diluent to transfer hydrogen. As the thermal cracking occurs, materials not suitable as donors will be cracked into the donor diluent boiling range and will reduce the concentration of the desired condensed ring aromatics, and some of the aromatics will be cracked out of the diluent boiling range. The amount of diluent bled and the amount of diluent makeup depend upon many factors, some of which are the diluent boiling range, the width of the diluent boiling range, the amount of hydrogen carried by the diluent, the residuum to diluent ratio, the cracking temperature, and the aromaticity of the residuum.

The spent diluent and the makeup thermal tar is hydrogenated in hydrogenator 18, using conventional methods and using preferably a sulfur insensitive catalyst such as nickel tungsten sulfide, cobalt molybdate, molybdenum sulfide, etc. The hydrogenation conditions are so adjusted that the diluent is only partially hydrogenated. It has been found that substantially complete hydrogenation destroys the effectiveness of the donor diluent. Sufficient hydrogen should be added to the diluent to make it serve effectively as a hydrogen donor but not to convert it substantially to naphthenes. Hydrogen is supplied

to the hydrogenator by line 19 and can originate from any convenient source. A particularly suitable source is the hydrogen from hydroforming operations.

Spent gas is removed from the hydrogenator by line 20, a portion of which may be recycled by line 21. The partially hydrogenated donor diluent is recycled by line 2 to the furnace.

A bleed is provided, by line 15, for the bottoms to prevent build-up of ash contaminants in the system. The amount of the bleed may be as high as 20%, based on fresh feed, but is generally about 1 to 5%. When the process is operated to obtain essentially complete residuum elimination, the minimum bottoms bleed is taken consistent with ash removal and removal of extremely refractory constituents which would eventually deposit as coke in the reactor.

The liquid level in the reactor is maintained at 50 to 90% of the reactor capacity by adjusting pressure, temperature, feed rate, diluent boiling range and the amount of bleed from the liquid phase. Since the diluent cracks to a much smaller extent than the residuum, it is apparent that there is a higher diluent to residuum ratio in the liquid phase of the reactor than in the feed. This results in the most efficient utilization of the diluent since it is present in high concentration where it is most needed, that is, for the liquid phase cracking of the most refractory components of the residuum needing a hydrogen donor diluent to prevent coking. For example, consider a feed consisting of 50% residuum and 50% diluent. With only a short contact time about one half of the residuum cracks readily and is removed from the vapor phase, thus increasing the diluent to bottoms ratio in the liquid phase from 1 to 1 up to 2 to 1.

The range of operating conditions pertinent to this invention are summarized in Table I. Table I also presents a specific example.

Table I

	Range	Example
Reactor Temperature, °F.	800 to 1,100	860
Reactor Pressure, p. s. i. g.	0 to 1,000	60
Reactor Feed Rate, w./v./hr.	0.5 to 10	2.0
Diluent/Residuum Ratio	1/20 to 1/1	49/51
Diluent Boiling Range, °F.	Above 430° F.	700-900
Diluent Bleed, Diluent Make-up, Percent of Diluent Recycled	up to 25	16.6
Bottoms Bleed, Percent of Feed	1 to 5	1.2
Hydrogenator Temperature, °F.	600 to 700	675
Hydrogenator Pressure, p. s. i. g.	300 to 3,000	550
Hydrogenator Feed Rate, w./v./hr.	0.1 to 5	0.5
Hydrogen Introduced in Diluent, s. c. f. per bbl. of diluent	100 to 1,000	450
1,000° F. + Conversion/pass, percent	80 to 98	98

<sup>1</sup> 1,000° F. + conversion is defined as: 100 vol. percent fresh feed minus vol. percent of products boiling above 1,000° F.

Table II presents an example of the results obtainable by the process of this invention when the process is operated in accordance with the example in Table I, using the particular feed stock indicated.

Table II

Inspections	12.9% West Texas Residuum	Hydrogenated 700/900° F. Thermal Tar Diluent
Elemental analysis, wt. percent:		
Carbon	85.28	90.24
Hydrogen	10.77	9.46
Sulfur	3.32	0.81
Nitrogen	0.52	
Oxygen	1.10	
H/C atomic ratio	1.51	1.25
Gravity, °API	7.5	8.0
Conradson Carbon, wt. percent	21.4	0.1
Ash at 800° C., wt. percent	0.18	
Aniline Point, °F.		91

Yields, percent on residuum + make-up diluent:

C <sub>3</sub> — gas, wt. percent.....	4
C <sub>4</sub> /430° F., vol. percent.....	24
430/700° F., vol. percent.....	62
900/1000° F., vol. percent.....	22
Bottoms, bleed, vol. percent.....	2

Although this process was described using a 700/900° F. diluent, it is to be clearly understood that any diluent boiling range may be used in the range of 430° and 1000° F. The main requirement is that the diluent consist predominantly of condensed ring, aromatic-naphthenic compounds which are only partially hydrogenated. For example, when heavy gas oil is desired for catalytic cracking feed stock the process may be operated with a 430/650° F. thermal tar diluent. In this case higher pressures would be used in order to take overhead only 430° F.-products, a larger bleed would be maintained from the liquid phase, and a 650/1000° F. gas oil would be separated as the major product. The process using a low boiling diluent is flexible as gasoline yields can be maximized in preference to catalytic charging stocks by using a 430/650° F. diluent and operating under severe cracking conditions in order to take the major portion of the products overhead. Another desirable alternative operation is obtained by using a diluent boiling in the range 800–1000° F. and taking overhead 800° F.-products, thereby maximizing middle distillate yields.

While the present process may be used for the mild thermal treatment of petroleum oils in the nature of visbreaking, it is more particularly suited to the substantially complete conversion of heavy oils. As an example, however, of a mild severity process, the residual oil can be treated at mild conversions, e. g., 50 to 80% 1000° F. conversions, using a high bottoms bleed. The bottoms bleed after removal of the spent diluent can be removed from the process and used as a residual fuel.

With reference to Figure II, a process will be described wherein the donor diluent is taken overhead as a vapor. As shown, the oil to be upgraded is introduced into the reactor by line 30 wherein it contacts and scrubs an ascending stream of spent diluent and conversion products. It passes downwardly to the base of the reactor and is mixed with substantial proportions of the hydrogen donor diluent. The liquid undergoing cracking may be heated by any suitable means. For example, a portion of the liquid can be continuously withdrawn by line 31, passed through a heater or furnace 32 and returned to the reactor by line 33. Steam or other substantially inert stripping gas may be admitted to the base of the reactor by line 34. This steam aids in the recovery of the spent diluent from the liquid.

The conversion products and the spent diluent, after having been scrubbed by the feed, pass upwardly to the fractionating tower and are condensed into various product streams. Light gases, naphthas and heating oils are removed by lines 35, 36 and 37, respectively. The spent donor diluent is removed by line 38 and transferred to a hydrogenator 39. A portion of this spent diluent may be cooled and recycled by line 40 to effect staged heat removal in the fractionation column. As before, a portion of this spent diluent stream may be bled from the process by line 41 and an equivalent amount of diluent material may be added to the process by line 42. As an alternative, the condensed ring structures in the diluent fraction may be concentrated before or after the addition of make-up thermal tar by a conventional means such as solvent extraction, thermal cracking, etc.

Hydrogen is admitted to the hydrogenator by line 43. The hydrogenated donor diluent is removed from the hydrogenator by line 44 and transferred to the heater 32 wherein it is heated to the reaction temperature. A bleed amounting to about 1 to 5% of the fresh feed is withdrawn from the base of the reactor by line 45. This

bleed may conveniently be adjusted such that the heat requirements of the process are balanced by use of the bleed as a fuel thereby eliminating the need for external fuel sources.

This particular arrangement having a vapor phase draw-off of the products and of the spent donor diluent is particularly suited to the processing of a hydrogen-deficient oil on a once-through basis. The residuum charged to the reactor can be maintained in the reactor until it is substantially converted to lighter distillates, thus avoiding the necessity for recycle operation. This arrangement is also suitable for extracting oils from shales, tar sands, etc. The solid material can be charged to the reactor and mixed with the donor diluent and thermally treated. The conversion products and spent donor diluent can then be removed overhead, and the spent solid discharged from the bottom of the reactor after being stripped.

While the examples have shown the separation and separate hydrogenation of the spent donor diluent, it is to be appreciated that the total overhead from the reactor can be hydrogenated. This alternative mode of operation will, however, be justified in only a few particular applications as the consumption of hydrogen will be relatively greater.

Having described the invention, what is sought to be protected by Letters Patent is succinctly set forth in the following claims:

1. A hydrogen donor diluent cracking process which comprises admixing a heavy hydrogen deficient petroleum, oil with 5 to 100 vol. percent of hydrogen donor diluent comprising partial hydrogenated predominately aromatic-naphthenic hydrocarbons boiling above 430° F., the precursor of said hydrogen donor diluent being selected from the group consisting of thermal tars, catalytic cycle stocks, extracts thereof, lube oil extracts and mixtures thereof and thermally cracking non-catalytically in a thermal cracking zone the mixture at a cracking temperature in the range of 800° to 1100° F. under liquid phase conditions to obtain 80 to 98% 1000° F. conversion of said hydrogen deficient oil while continuously removing gasiform conversion products boiling below the boiling range of said diluent, whereby the ratio of unconverted hydrogen donor diluent to unconverted hydrogen deficient oils in the liquid mixture undergoing cracking is substantially increased and efficient utilization is made of unconverted hydrogen donor diluent.

2. The hydrogen donor diluent cracking process claimed in claim 1 comprising continuously withdrawing liquid from said thermal cracking zone, separating the liquid to obtain spent hydrogen donor diluent, adding makeup diluent precursor as above described thereto, partially hydrogenating a major portion of the separated material including said makeup diluent precursor to regenerate the hydrogen donor diluent, and returning the material so hydrogenated to said thermal cracking zone.

3. The process of claim 2 wherein said gasiform conversion products and withdrawn liquid are separated in a common fractionation zone to obtain product fractions and spent diluent, and recycling a major portion of the residue from said fractionation zone to said thermal cracking zone for further treatment.

4. A process for the conversion of heavy hydrocarbonaceous petroleum materials which comprises the steps of: introducing a charging stock and a hydrogen donor diluent boiling in a range within the limits of 430° to 1000° F. into a thermal cracking zone, maintaining said charging stock and said hydrogen donor diluent therein under liquid phase hydrogen donor diluent, non-catalytic, cracking conditions to obtain relatively lighter vaporous products, continuously withdrawing overhead said vaporous products, separately withdrawing liquid comprising spent diluent and unconverted portions of said charging stock from said thermal cracking zone,

passing the liquid so withdrawn and said vaporous products to a common separation zone, separating therein said spent diluent and adding thereto makeup precursor diluent selected from the group consisting of thermal tars, catalytic stocks, extracts thereof, lube oil extracts, and mixtures thereof, partially hydrogenating said spent diluent and returning the material so partially hydrogenated to said thermal cracking zone.

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