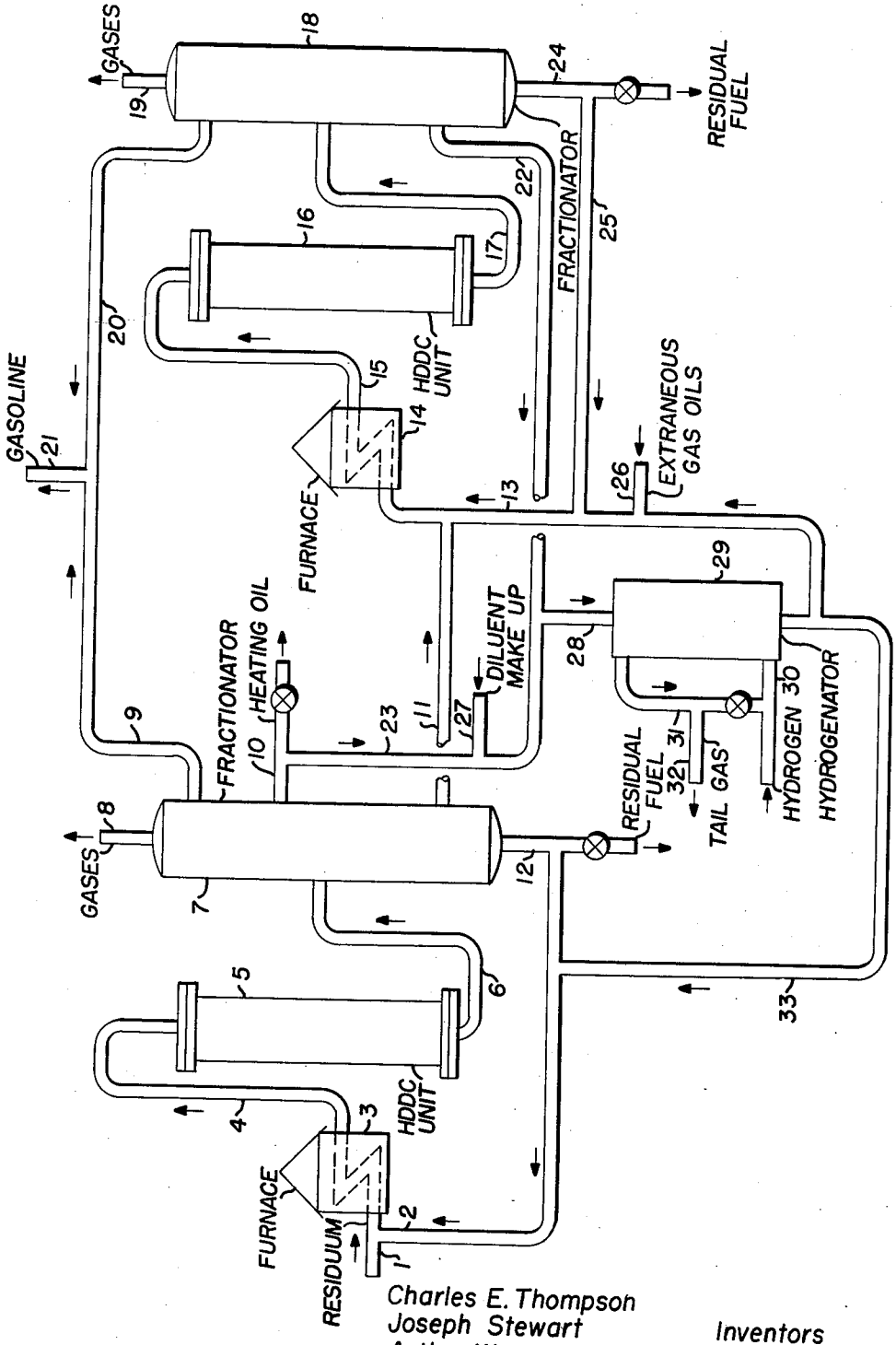
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TWO-STAGE HYDROGEN DONOR DILUENT CRACKING PROCESS

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TWO-STAGE HYDROGEN DONOR DILUENT CRACKING PROCESS

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This invention pertains to the conversion of hydrocarbon oils by hydrogen donor diluent cracking. More particularly, it is concerned with the upgrading of petroleum oils, particularly heavy high-boiling oils such as vacuum residua, by thermal cracking the oil in the presence of a hydrogen donor diluent. According to this invention, low value hydrogen deficient oils having coke forming propensities during thermal cracking are converted to maximum yields of gasolines by a two-step or stage HDDC process.

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

This HDDC process has been envisaged mainly for the production of catalytic cracking quality gas oils from waste materials such as heavy residua. It had been felt that to produce motor fuel quality gasolines directly by this process would be highly uneconomical. From further thought and experimentation, it has now been found that this is not the case and that this HDDC method may advantageously be used for the direct production of gasolines. By staging the process, as will appear, superior and unexpected results are obtained.

The present invention proposes a two-step hydrogen donor diluent cracking process which comprises the conversion of a heavy oil by HDDC to secure naphthas and gas oils, and then further converting the gas oils so produced by a second HDDC stage. A relatively low boiling hydrogen donor diluent is used in the second stage. This staging results in an unusually high selectivity of the process to the production of gasolines as optimum conversion conditions can be maintained in each stage. The importance of maintaining optimum conditions has not been fully appreciated heretofore.

The present process obviates the need for catalytic conversion of the gas oil from the first HDDC stage. Although catalytic cracking is a process of much value, it results in the useless degradation of a gas oil being converted to 5 to 10 wt. percent carbon and to 15 to 25% light gases. This diminishes the yield of useful liquid products. In the present process, the gas oil from the first stage is converted in the second stage to high yields of gasolines with very low gas yields and with production of a negligible amount of carbon. The gasoline so produced is readily amenable to being reformed, preferably by hydroforming, to yield a high quality motor fuel product.

This two-step process fundamentally differs from a single-stage process in which material boiling above the desired gasoline boiling range is recycled to obtain high conversions. In a single-stage process, if materials heavier than gasolines, e. g., boiling above 430° F., are recycled to obtain increased yields then optimum conversion conditions cannot be observed because it is necessary to meet conditions required for the conversion of the heavy oil that is charged to the cracking process. Thus in a single-stage process the product selectivities with respect to gasoline production leaves much to be desired.

It is an object of this invention to upgrade heavy hydrocarbon oils. It is another object to convert high boiling hydrogen deficient material such as petroleum residua to maximum quantities of gasoline boiling range product. A more particular object is to convert heavy oils in a two-stage hydrogen donor diluent cracking process.

Other objects and advantages of this invention will more clearly appear as this description proceeds during which the attached drawing, forming a part of this specification, is discussed in detail. The attached drawing depicts a two-stage HDDC process wherein hydrogen donor diluents of common boiling range are used in each step.

In its more specific aspects, the present invention is concerned with a petroleum residua conversion process which comprises subjecting a residuum to hydrogen donor diluent cracking, using a hydrogen donor diluent boiling in a range within the limits of 400° to 700° F., with recycle of the bottoms material whereby a gasoline product and distillate gas oils are obtained, and further converting the distillate gas oils in a second conversion zone by hydrogen donor diluent cracking using additional amounts of the hydrogen donor diluent with recycle of the bottoms material whereby additional amounts of gasoline product are obtained.

Charging stocks for the present invention are preferably 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 −5° to 20°, Conradson carbons of 5 to 50 wt. percent, and initial boiling points above about 850° to 1100° F. This invention is, however, capable of enjoying broader applications. Thus coal tars, shale oils, tars asphalts, etc. may also be processed.

The sources of the aromatic-naphthenic oil that is partially hydrogenated to secure the hydrogen donor diluent have previously been described. In particular, thermal tars obtained by the thermal cracking of catalytic cycle stocks yield excellent donor diluents. Virgin gas oils, certain lube oil extracts, extracts of catalytic cycle stocks, heavy cycle stocks themselves, or bottoms from catalytic cracking can also serve as a source of the donor diluent. The prime consideration in the selection of a hydrogen donor diluent is that it 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 except for loss of hydrogen. The condensed ring structures can be recovered and regenerated by partial hydrogenation. While a major proportion of the donor diluent can be continuously reused, there will normally be some loss of the donor diluent and this loss is made up from extraneous sources.

While it is preferred to use relatively low boiling hy-

drogen donor diluents of the same boiling range in each of the conversion zones, the diluent used in the first conversion zone may have a boiling range within the limits of 400° to 1000° F., e. g., a diluent boiling in the range of 700° to 900° F. may be used. In the first zone wherein the heavy residuum is handled, the diluent boiling range must be selected such that the diluent will sufficiently solubilize and peptize the residuum in this zone, particularly when recycle operation is practiced. The use of a low boiling diluent in the first zone may encounter the difficulty of failing to completely solubilize the material charged since the disparity between boiling ranges may be too great. In the second stage, the diluent has preferably a boiling range within the limits of 400° to 700° F., e. g., a diluent boiling in the range of 430° to 600° F. may be used. This boiling range is immediately above that of the gasoline product. This is desirable because any of the highly aromatic diluent which is cracked in the process yields gasoline and aromatics which are high octane components of gasoline. Also diluent boiling in this range is desirable because in a recycle operation the diluent is separated by distillation and the remaining product recycled, whereas, in order to recover a high boiling diluent, the gas oil boiling below the diluent must be distilled also.

It is advantageous to use hydrogen donor diluents of a common boiling range, e. g., 430° to 650° F., in each zone. This simplifies the replenishment of the diluent and the regeneration of the diluent by partial hydrogenation because a single common hydrogenation zone may be used. This arrangement is illustrated in the attached drawing. It is to be pointed out that diluents of different boiling ranges can very well be used. For example, 700° to 900° F. boiling range diluent can be used in the first stage and a 550° to 700° F. boiling range diluent can be used in the second stage. Separated hydrogenation zones may be used for each diluent stream, particularly when they have different boiling ranges.

The operating conditions applicable to the following description of the attached drawing are conveniently summarized in Table I, presented hereinafter.

A heavy oil feed in line **1** is admixed with a hydrogen donor diluent and a recycled bottoms fraction supplied by line **2**. The resulting mixture is then subjected to hydrogen donor diluent cracking in conventional equipment which may include a coil and/or drum. As shown, the mixture is heated by furnace **3** to conversion temperatures and then transferred by line **4** to a soaking or HDDC zone **5**. The mixture is held resident for a time sufficient to obtain the desired degree of conversion. The cracked mixture is then transferred by line **6** to a fractionator **7** or equivalent separation system. Besides gases separated and removed by line **8** and gasoline product removed by line **9**, a spent hydrogen donor diluent fraction is recovered by line **10**. The gas oil product of the first stage boiling above the end point of the hydrogen donor diluent is removed by line **11**. The remaining bottoms which may have an initial boiling point above about 900°–1150° F., is removed by line **12**. To prevent build-up of an undue amount of refractory constituents and ash constituents in the recycle stream, it is desirable to bleed approximately 1 to 10% of the bottoms from the process. The remainder is recycled by line **2** as previously described.

The amount of this bleed and the amount of other bleeds described hereinafter may conveniently be made to be just sufficient to meet the fuel requirements of the process. It may, however, be desired to produce a residual fuel product to meet market demands. Accordingly, the degree of conversion in each stage can be reduced somewhat to obtain the desired residual fuel product.

The gas oil in line **11** which may have a boiling range within the limits of 650° to 1150° F. is admixed with hydrogen donor diluent having the same boiling range as the diluent used in the first stage, and with a recycled bottoms fraction from the second stage, supplied by line **13**. The mixture is heated in furnace **14** and transferred by line **15** to a soaking drum **16**. After a sufficient residence time, the conversion products are transferred by line **17** to fractionator **18**. Light gases are vented from the fractionator by line **19**. The gasoline product is removed by line **20**, combined with the contents of line **9** and removed from the process as product via line **21**. The spent hydrogen donor diluent is recovered by line **22** and mixed with the recovered hydrogen donor diluent from the first stage in line **23**. The remaining portion of the second stage conversion products boiling above the end boiling point of the diluent, e. g., above 650° F., is recycled via lines **24**, **25** and **13**. Approximately 2 to 10 vol. percent of this recycled material, based on the gas oil feed to the second stage, may be bled from the process as residual fuel by line **24**. It will be apparent to those skilled in the art that instead of recycling all material boiling above the end boiling point of the diluent, the distillate gas oils only may conveniently be separated and recycled, leaving a heavy bottoms fraction which can be withdrawn from the process as a residual fuel product.

The second stage may also conveniently be used to concurrently convert extraneous gas oils to gasolines which can be supplied to the second stage via lines **26** and **13**. These extraneous gas oils may comprise virgin gas oils or less valuable materials such as lube oil extracts, thermal tars, catalytic cycle stocks, coker gas oils, etc. of suitable boiling range.

Materials not suitable as hydrogen donors will be cracked into the diluent boiling range and some of the aromatic-naphthenic molecules will be lost by cracking. To maintain the hydrogen transfer properties of the diluent, it is desirable, in some instances, to remove from the process some of the spent diluent and to replace it with an equivalent amount of material from the sources previously indicated. This may be done by line **10** and the addition may be made by line **27**. In many cases, the feed streams to the process will supply a sufficient amount of aromatic-naphthenic materials or hydrocarbons that will reduce to aromatic-naphthenes such that make-up diluent is not required. This is particularly true when the naphtha product of the process is undercut somewhat (to about 375°–400° F.) to obtain a larger amount of diluent.

The effective aromaticity of the diluent may also be maintained by suitable concentrating processes. Thus the contents of line **23** and/or **22** may be subjected to extraction processes, e. g., propane or sulfur-dioxide extraction, to concentrate the desirable aromatics therein. Alternatively, the material may be mildly thermally cracked to crack out molecules not having hydrogen donor properties such as paraffins, or it may be catalytically aromatized to increase the aromaticity of the diluent. These alternatives are not shown on the attached drawing.

The contents of lines **22** and **23** are transferred by line **28** to a hydrogenation zone **29** wherein the spent donor diluent is regenerated by partial hydrogenation. It is important that the diluent be only partially hydrogenated as complete or substantially complete conversion of the aromatic-naphthenes to naphthenes will substantially reduce or eradicate the effectiveness of the material to serve as a hydrogen donor. This is somewhat converse to the view formerly held in the prior art.

The spent diluent is hydrogenated in a hydrogenator **29** using conventional methods and using, preferably, a sulfur insensitive catalyst such as nickel-tungsten-sulfide, cobalt molybdate, molybdenum sulfide, etc. Sufficient hydrogen is added to the diluent to make it serve as an effective hydrogen donor. Hydrogen is supplied to the hydrogenator by line **30** and may originate from any convenient source such as from the electrolysis of water, gasification of carbonaceous material, etc. A particularly suitable source is the hydrogen from a hydroforming

operation wherein the octane number of the gasoline is improved. The hydrogen gas is recycled via line **31**. A portion of it is removed from the process by line **32** and replaced with an equivalent amount of higher purity hydrogen supplied by line **30**.

The hydrogenated material is then removed by line **33** from vessel **29** and a portion of it is recycled by line **13** as previously described and the remainder is transferred to the first cracking stage by lines **33** and **2**.

Table I summarizes the pertinent operation conditions applicable to the process depicted in the attached drawing and presents a specific example thereof. Table II presents a specific example of the products obtainable from the feed stock indicated when the process is operated in accordance with the example of Table I.

TABLE I

Operating conditions

	Range	Example
Residuum Conversion Unit:		
Temperature, °F	700 to 1,000	860.
Pressure, p. s. i	14 to 800	400.
Combined feed rate,[1] v./v./hr.	0.25 to 15	4.0.
Diluent/fresh residuum ratio, wt./wt.	0.2 to 2	1.
Diluent boiling range, °F	Within limits of 400°–1,000°.	430°–650°.
Diluent make-up, vol. percent of fresh residuum.	2 to 30	28.[2]
Recycle bottoms rate, vol./vol. fresh residuum.	0.5 to 2	1.[3]
Bottoms bleed, vol. percent of fresh feed.	1 to 5	2.
1,000° F. — conversion,[4] vol. percent.	40 to 70	50.
Gas Oil Conversion Unit:		
Temperature, °F	750 to 1,000	940.
Pressure, p. s. i	50 to 1,000	400.
Combined feed rate,[1] v./v./hr.	0.5 to 10	4.0.
Diluent/gas oil ratio, wt./wt.	0.2 to 2	0.5.
Diluent boiling range, °F	Within limits of 400° to 700° F.	430°–650°.
Recycle bottoms rate, vol./vol. gas oil.	0.25 to 2	0.4.[5]
Extraneous gas oil addition rate, if any, vol./vol. gas oil from residuum unit.	0.1 to 2	0.
Gas oil boiling range, °F	Within limits of 650°–1,000°.	650°–1,000°.
Bottoms bleed, vol. percent gas oil feed.	0.2 to 5	3.
430° F. minus conversion,[6] vol. percent.	50 to 90	50.
Hydrogenation Unit:		
Catalyst		Nickel Tungsten Sulfide.
Temperature, °F	600 to 700	675.
Pressure, p. s. i. g	300 to 3,000	550.
Feed rate, v./v./hr.	0.1 to 5	0.5.
Hydrogen introduced into diluent, s. c. f. bbl. of diluent.	100 to 1,000	450.

[1] Including diluent and recycle, if any.
[2] Considering all diluent make-up as chargeable to residuum unit.
[3] 1,000° F.+ bottoms.
[4] 1,000°F.— conversion is defined as: 100 vol. percent fresh residuum less products boiling above 1,000° F., excluding coke.
[5] 650° F.+ bottoms.
[6] 430° F.— conversion is defined as: 100 vol. percent fresh gas oil feed from residuum unit plus extraneous gas oils, if any, less products boiling above 430° F., excluding coke.

TABLE II

Feed Inspections	12.9% West Texas Residum	430/650° F. Make-up Diluent
Elemental analysis, wt. percent:		
Carbon	85.28	88.02
Hydrogen	10.77	11.12
Sulfur	3.32	0.68
Nitrogen	0.52	
Oxygen	1.10	
H/C atomic ratio	1.51	1.51
Gravity, °API	7.5	22.4
Conradson carbon, wt. percent	21.4	0.01
Ash at 800° C., wt. percent	0.18	
Aniline point, °F		117.7
Yields, Percent on Residuum:		
C_3-Gas, wt. percent	13.9	
C_4/430° F., vol. percent	[1] 90.3	
650° to 1,000° F., vol. percent	2.8	
Residual fuel, vol. percent	2.0	
Coke, wt. percent	2.1	

[1] 67 Res. O. N. clear.

The above Table II is for recycle operation. For operation on a once through basis, the following data, presented in Table III were obtained. A 650° to 1000° F. gas oil from HDDC of West Texas vacuum residuum, identified in Table II, was blended with one half its weight of partially hydrogenated 430°–650° F. thermal tar and cracked in a coil at 940° F., 400 p. s. i. g. and at a feed rate of 4.1 v./v./hr. The product yields are given below:

TABLE III

	Yields on gas oil
Coke, wt. percent	3.5
C_3—, wt. percent	9.3
C_4—, 430° F., vol. percent	54.6
430–650° F. diluent, vol. percent	9.9
650–1000° F., vol. percent	24.5

The coke yield of 3.5 percent is low considering that the conversion of gas oil to lighter products was 75.5 volume percent. The selectivity to gasoline was 72.3 volume percent.

The results in Table III are based on a single pass operation. Recycle operations would, of course, give a higher ultimate yield of gasoline. The yield of coke is negligible if the conversion of gas oil per pass is reduced to 50 percent. This also lowers the yield of dry gas formed in the process.

Numerous variations of this invention will be apparent to those skilled in the art. Having described this invention, what is sought to be protected by Letters Patent is succinctly set forth in the following claims.

What is claimed is:

1. A hydrocarbon conversion process which comprises mixing 1 volume of a heavy oil with 0.2 to 2 vol. of a hydrogen donor diluent containing major proportions of aromatic-naphthenics boiling in a range within the limits of 400° and 1000° F. and with 0.5 to 2 volumes of a recycled bottoms fraction boiling above about 900° F., subjecting the mixture to conditions of hydrogen donor diluent cracking including a pressure in the range of 14 to 800 p. s. i., a temperature in the range of 700° to 1000° F., and a combined feed rate in the range of 0.25 to 15 v./v./hr. to obtain 1000° F.— conversions of said oil in a range of 40 to 70 vol. percent, separating the mixture so treated to secure products boiling below the boiling range of said aromatic-naphthenes, spent hydrogen donor diluent, gas oils, and said bottoms fraction, regenerating said spent hydrogen donor diluent by partial hydrogenation in a catalytic hydrogenation zone and recycling the material so hydrogenated, admixing said gas oils with 0.2 to 2 vols. of a relatively low boiling hydrogen donor diluent per vol. of gas oil, said relatively low boiling hydrogen donor diluent comprising major proportions of aromatic-naphthenes boiling in a range within the limits of 400° to 700° F., and a recycled second bottoms fraction boiling above about 650° F., subjecting the resulting mixture to conditions of hydrogen donor cracking including a pressure in the range of 50 to 1000 p. s. i., a temperature in the range of 750° to 1000° F., and a combined feed rate in the range of 0.5 to 10 v./v./hr. to obtain a 430° F.— conversion of said gas oil in the range of 50 to 90 vol. percent, separating the mixture so treated to obtain products, to recover spent relatively low boiling hydrogen donor diluent, and to secure said second bottoms fraction, regenerating said spent relatively low boiling hydrogen donor diluent by partial hydrogenation in a catalytic hydrogenation zone and recycling and admixing the material so hydrogenated with said gas oils.

2. The process of claim 1 wherein said hydrogen donor diluent and said relatively low boiling hydrogen donor diluent have substantially the same boiling range and are regenerated in a common catalytic hydrogenation zone.

3. The process of claim 1 wherein 0.1 to 2 vols. of extraneous gas oils per vol. of said gas oils are added to said gas oils and treated therewith.

4. The process of claim 1 wherein 1 to 5 vol. percent based on said heavy oil, of said bottoms fraction is bled from said process, wherein 0.2 to 5 vol. percent based on said gas oil of second bottoms fraction is bled from said process, wherein 2 to 30 vol. percent based on said heavy oil, of said spent hydrogen donor diluent is replaced with make-up and wherein 2 to 20 vol. percent, based on said gas oil, of said spent relatively low boiling hydrogen donor diluent is bled from said process and replaced with make-up.

5. A petroleum residua conversion process to obtain maximum gasoline yields which comprises subjecting a residuum to hydrogen donor diluent cracking using a hydrogen donor diluent boiling in a range within the limits of 400° F. to 700° F., at 1000° F.— conversions in the range of 40 to 70 vol. percent with recycle of the bottoms material whereby a gasoline product and distillate gas oils boiling above the end boiling point of said hydrogen donor diluent up to about 1150° F. are obtained, further converting said distillate gas oils in a second conversion zone by hydrogen donor diluent cracking using additional amounts of said hydrogen donor diluent at 430° F.— conversions in the range of 50 to 90 vol. percent with recycle of the bottoms material whereby additional amounts of gasoline product are obtained.

6. The process of claim 5 wherein the bottoms material from said second conversion zone boiling above the end boiling point of said hydrogen donor diluent are separated to obtain a gas oil product, the remainder, excepting for small bleed, being recycled.

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