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HYDROGEN DONOR DILUENT CRACKING PROCESS

Filed March 5, 1956

2 Sheets-Sheet 1

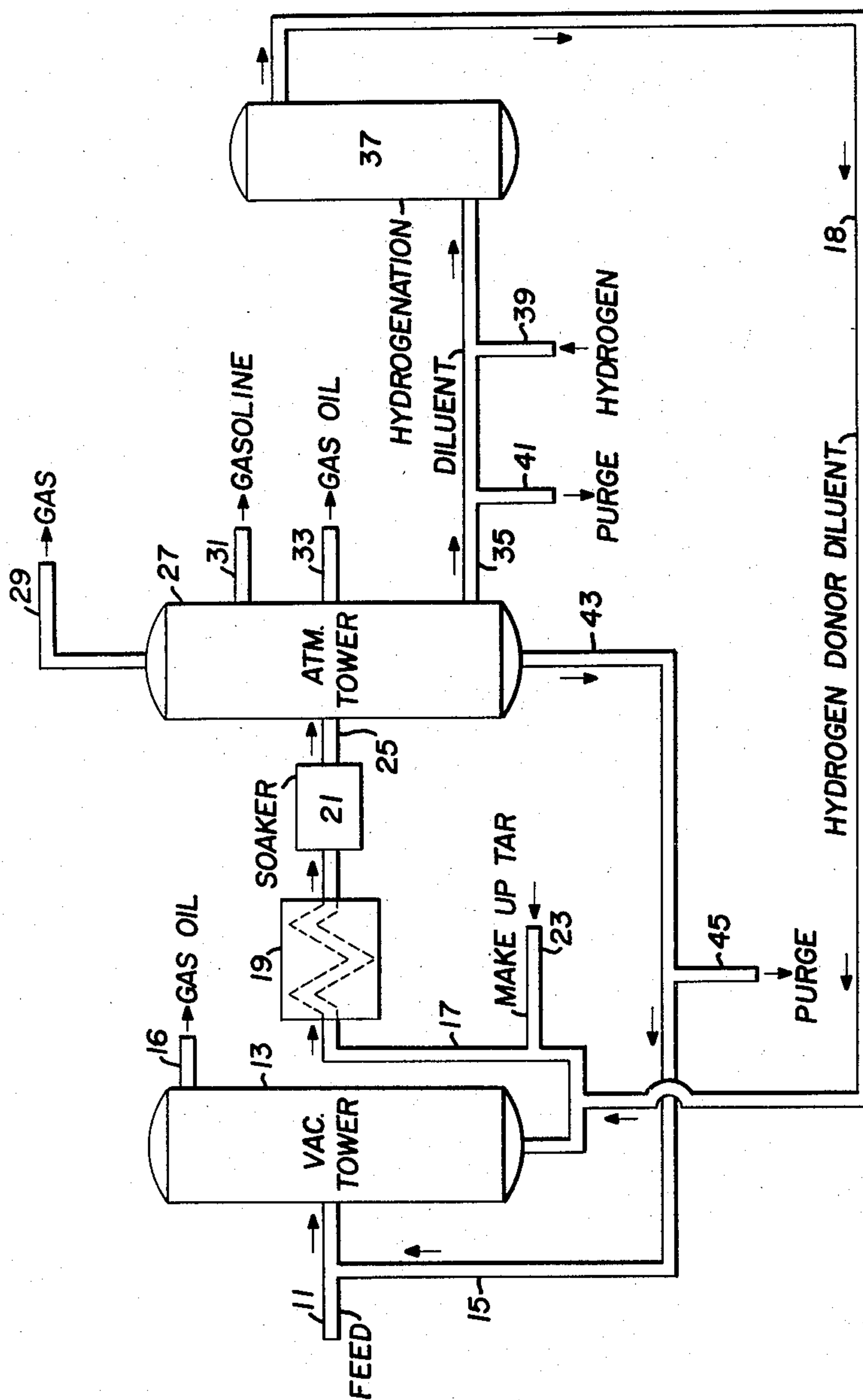


FIGURE - I

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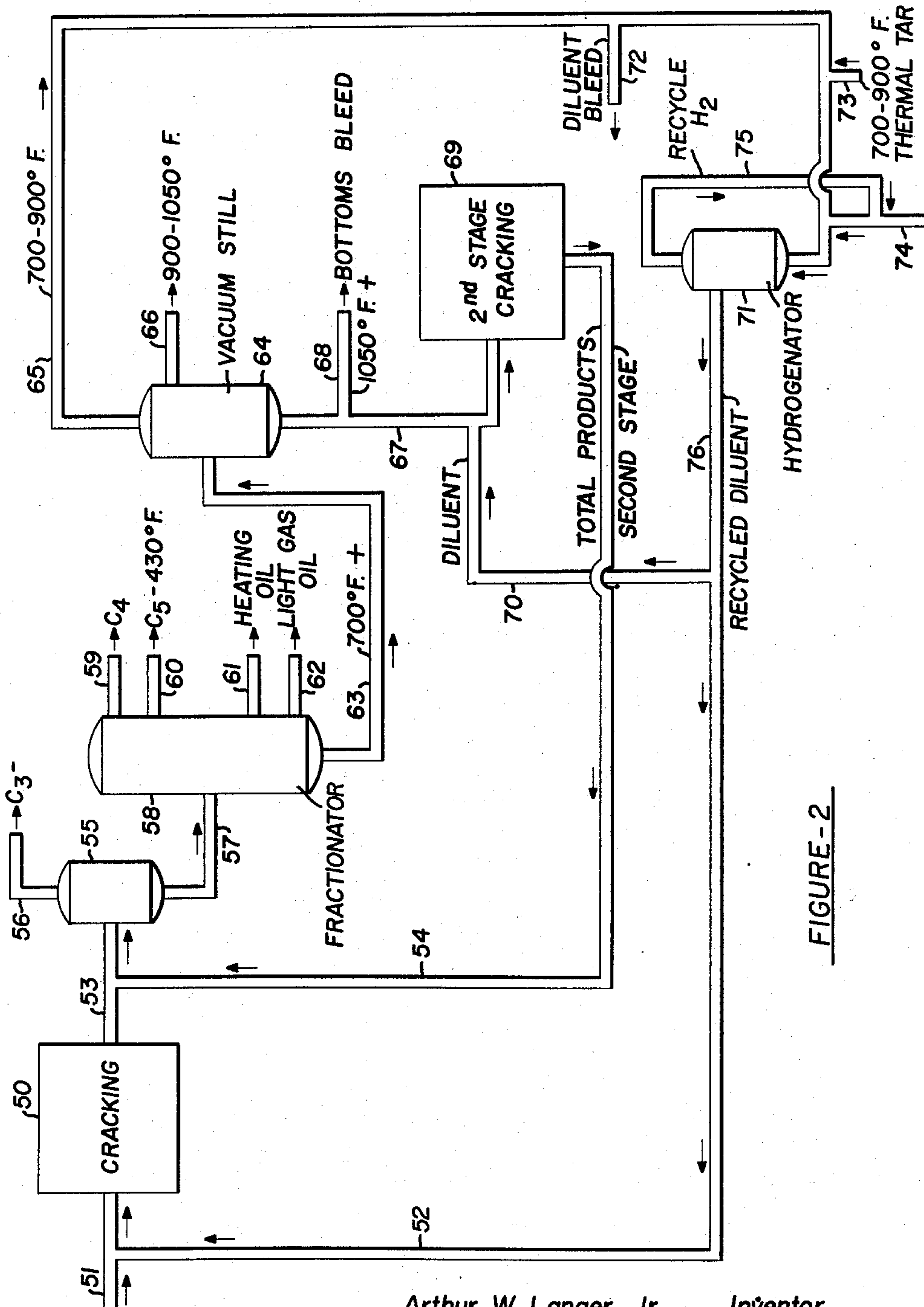


FIGURE - 2

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2,953,513

HYDROGEN DONOR DILUENT CRACKING PROCESS

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15 Claims. (Cl. 208—56)

This invention relates to the conversion of heavy hydrocarbon oils using an improved hydrogen donor diluent. It is more particularly concerned with a method of simultaneously cracking and hydrogenating heavy oils by using a select high-boiling hydrocarbon fraction that displays hydrogen donor properties upon partial hydrogenation.

This application is a continuation-in-part of "Upgrading of Heavy Hydrocarbon Oils," Serial No. 365,335, filed July 1, 1953, by the present inventor, now abandoned.

It is known by the art to upgrade hydrogen deficient oils, such as vacuum residua and asphalts, to more valuable liquid distillates by thermally cracking in liquid phase the hydrogen deficient material in admixture with a hydrogen donor diluent. The hydrogen donor diluent is a material, aromatic-naphthenic in nature, that 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. One of the principal advantages of the hydrogen donor diluent cracking (HDDC) process is that it can convert heavy oils, not amenable to other conversion processes, at high conversions in the absence of a catalyst and with the formation of little, if any, coke. The gas oils obtained by this process are particularly amenable to further conversion, such as by catalytic cracking.

With the exception of temperature, conventional hydrogen donor diluent cracking conditions are used in the practice of this invention. These include a diluent/feed ratio in the range of 0.1 to 5 vol./vol., a combined feed rate in the range of 0.1 to 15 v./v./hr. (or residence time of 0.25 to 5 hrs.), and a pressure in the range of 0 to 1000 p.s.i., preferably a pressure sufficient to maintain liquid phase conditions. The temperature during cracking is discussed infra.

It is believed that the hydrogen donor diluent functions by conveying loosely held hydrogen into the cracking zone, and that this hydrogen is taken up by the pyrolytic products or molecular fragments obtained by the thermal cracking of the acceptor oil. In continuous operation, it is desirable to recover the diluent, as by fractionation, from the thermal cracking zone effluent, to rehydrogenate it, and return it to repeat the cycle. It is often necessary in such recycle operations, because of imperfect fractionation and because of diluent loss by cracking, to supply from an extraneous source a hydrocarbon fraction containing a high proportion of hydrogen donor or aromatic-naphthenic molecules.

Hydrogen donors proposed by the art have been rela-

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tively low boiling, pure, and expensive compounds such as naphthalene, tetralin, decalin, anthracene, and the like. Because of their expense and because of other difficulties inherent in the use of low-boiling diluents, the hydrogen donor diluent cracking (HDDC) process has not heretofore been considered practical.

It has now been discovered that a superior hydrogen donor diluent for upgrading heavy oils can be obtained from certain select low value, normally surplusage, high boiling refinery streams. More particularly, it has been found that certain distillate thermal tars, more fully described below, boiling above 700° F., will, upon partial hydrogenation, produce an excellent hydrogen donor diluent material. It is surprising that such impure, refractory and low value thermal tars yield a material that serves as a hydrogen donor and in fact, display superiority over previously proposed hydrogen donors. The thermal tar hydrogen donor diluents of this invention achieve better hydrogen utilization and result in unexpected increases in yields and selectivities.

Broadly, the hydrogen donor diluent precursor used in this invention is a distillate material derived from hydrocarbon fractions that have been substantially cracked, either thermally or catalytically, and are, therefore, highly aromatic and refractory. Preferred precursor materials have a boiling range within the limits of 700 to 1100° F., and an A.P.I. gravity below 20°. Especially preferred, however, are thermal tars obtained by extensive thermal cracking of high boiling surplusage refinery streams.

By thermal tars, as used in the specification and claims, is meant the product having the above-described characteristics obtained by thermally cracking at a temperature in the range of 800 to 1600° F., a pressure in the range of 0 to 1000 p.s.i., and at a 430° F.—conversion above 20 wt. percent, normally surplusage, low value, high boiling refinery materials including: clarified oils and cycle stocks boiling above 900° F. and including residual fractions obtained by the catalyst cracking of gas oils; solvent extracts obtained during the processing of lube oil stocks; asphalt precipitates obtained from deasphalting operations; high boiling bottoms or residua obtained during vacuum distillation of petroleum oils; aromatic extracts obtained by the treatment of distillates or residua as with furfural, sulfur dioxide, phenol, dichloroethyl ether; heavy fractions from coking operations; and the like. It is important that the precursor thermal tars have an aromatic ring content above 40 wt. percent in the 700° F.+ fraction, and it is especially preferred that the aromatic ring content be above 50 wt. percent.

It has been found, contrary to indications in the prior art, that there is an optimum level of partial hydrogenation of the hydrogen donor diluents that results in the greatest and most efficient utilization of the diluent. Fully condensed structures (aromatics) are ineffective as hydrogen donors. Completely hydrogenated condensed ring molecules such as a decahydronaphthalene, while perhaps transferring some hydrogen, transfer only a negligible amount. It is the aromatic-naphthenes having one or more aromatic nuclei giving instability to the molecule, which serve as superior hydrogen donors. By partial hydrogenation is meant an extent of hydrogenation sufficient to introduce on the average one to three hydrogen molecules into the aromatic-naphthenic donor

molecule, while leaving one or more rings unhydrogenated. This results in a diluent having a hydrogen to carbon atomic ratio in the range of 0.7 to 1.6.

The select hydrogen donor diluent of this invention, besides being considerably cheaper than prior art diluents, has several surprising advantages. Because it is high boiling, a substantially lower operating pressure can be used to maintain liquid phase conditions. It solubilizes better with the heavy, usually viscous, oils being upgraded such that the oil molecules and the donor molecules are in intimate contact and greater efficiency is obtained. Prior art donor diluents such as tetralin are much less efficient despite having more available hydrogen per weight. The heavy thermal tar diluent of this invention customarily transfers substantially all of the hydrogen introduced into it in the hydrogenation stage and little, if any, free hydrogen appears in the products as is customary when using a tetralin diluent.

These and other innate characteristics of the hydrogen donor diluent of this invention result in a superior heavy oil hydrogen donor diluent cracking process that obtains improved and unexpected results.

The hydrogen donor diluent cracking process is customarily used for the substantially complete conversion or reduction of residual oils that contain catalyst contaminating constituents, such as coke formers and metal salts. It can well be used in milder types of conversion process such as vis-breaking to reduce a refinery's production of residual fuel by preventing formation of severity limiting M.N.I. or H.F.S. content, or to increase the pumpability of extremely heavy crudes or fractions therefrom. The hydrogen donor diluent cracking process also can be used to destroy carcinogenic stocks such as highly aromatic catalytic cracking cycle stocks and the like. It has good potential in obtaining further distillate materials from asphalts and tars and for increasing the production of lube oils by converting the solvent extracts normally obtained during lube oil processing.

In light of the above, the heavy oil feed stocks which are charged to the process of this invention include: petroleum residua containing constituents non-vaporizable without cracking, and usually containing deleterious catalyst contaminating compounds; extracts, asphalts, tars, shale oils, whole crudes, synthetic heavy oils, and the like. The most beneficial use of the hydrogen donor diluent cracking process is in the conversion of heavy oils not amenable to other means of upgrading and characterized by a Conradson carbon content above 15, a boiling point above 900° F., a gravity in the range of -5 to 20° A.P.I., and a sulfur content above 3 wt. percent.

In brief compass, this invention proposes a conversion process wherein a heavy hydrogen deficient oil is admixed with an improved hydrogen donor diluent and subjected to conditions of non-catalytic, liquid phase hydrogen donor diluent cracking in the absence of extraneous free hydrogen. The improved diluent of this invention comprises a distillate material boiling above 700° F. which has been partially hydrogenated to have a hydrogen-carbon ratio in the range of 0.7 to 1.6 and contains predominate proportions of polycyclic aromatic-naphthenes having at least one aromatic ring. The preferred distillate donor precursor is a thermal tar obtained by the extensive thermal cracking of surplusage high boiling refinery streams.

The following description of the drawings and examples will serve to make this invention clear.

In the drawings, Figure 1 depicts schematically a simplified embodiment of the hydrogen donor diluent cracking process of this invention.

Figure 2 illustrates an alternative embodiment involving two conversion stages.

Referring now to Figure 1, a viscous hydrocarbon oil feed, typified by a 16% West Texas residuum, is supplied by a line 11 to a vacuum tower 13 where it is vacuum stripped to remove any available gas oil. The

feed is blended with a recycled bottoms fraction supplied through line 15, explained below, and both are subjected to the vacuum stripping. The gas oil is taken off through a line 16.

The stripped mixture then passes from tower 13 through a line 17 where it is mixed with 0.1 to 5, preferably 0.25 to 4 volumes of a high boiling hydrogen donor diluent per volume of stripped material supplied by line 18. The mixture is then passed through a heating coil 19 and a soaker 21 where it is subjected to conditions of hydrogen donor diluent cracking.

Make up thermal tar, the hydrogen donor diluent precursor, preferably a thermal tar fraction boiling between about 700 and 900° F. and comprising predominate proportions of aromatic-naphthenes, is supplied if necessary through a line 23 joining line 17, prior to the thermal cracking step, although it can be admitted elsewhere to the process if desired.

The cracked mixture from the soaker 21 is led through line 25 to an atmospheric distillation column 27 where it is fractionated to obtain dry gases (C₃ or C₄ and lower plus hydrogen) from the top through line 29, a C₅ to 430° F. (gasoline) cut through line 31, a 430 to 700° F. gas oil through line 33, and a 700 to 900° F. fraction through line 35. The latter is passed to a hydrogenation zone 37, with hydrogen being supplied to the zone through line 39. A portion of this fraction may be purged from the system through a line 41 to prevent undue build-up of impurities or objectionable ingredients which do not contribute to the hydrogen donor diluent function.

The 900° F.+bottoms from tower 27 are recycled through line 43 which connects with line 15, as mentioned above. A portion of these bottoms may be purged through a line 45 to prevent undue build-up of ash forming and other objectionable materials.

The 700-900° F. fraction is hydrogenated using conventional conditions by introducing about 200 to 1000 cubic feet of hydrogen per barrel of the fraction, and passing the mixture over a suitable hydrogenation catalyst. Because most such fractions contain appreciable quantities of sulfur, it is usually preferable to employ a relatively sulfur-insensitive catalyst, such as molybdenum sulfide or a tungsten nickel sulfide, as is well known in the art. Conventional hydrogenation pressures, e.g. 100 to 1000 p.s.i.g. or more, may be used. The conditions, in any case, should be so chosen that the diluent is only partially hydrogenated. It should pick up enough easily removable hydrogen to be effective as a donor, but not enough to approach saturation or to convert it substantially to naphthenes. With a 700 to 900° F. thermal tar of average effective molecular weight around 300, hydrogen consumption may run from about 200 to 800 standard cubic feet per barrel (s.c.f./bbl.). The hydrogenated diluent is returned through line 18.

EXAMPLE 1

In a typical operation, using the above system on a 12.9 West Texas residuum, the following results were obtained, using a 1 to 1 feed/diluent ratio:

Table I

Diluent.....	None	Thermal Tar	Partially Hydrogenated Thermal Tar
Feed rate, v./v./hr.....	3.0	2.0	2.02
Temperature, ° F.....	820	840	840
Conversion, on residuum (Vol. percent to 1000° F.—plus coke).....	30	28	57.4
Coke yield, percent by wt.....	2.5	2.0	0.1

The thermal tar was a 700-900° F. fraction obtained from the thermal cracking of clarified oil from a gas oil fluid catalytic process. It had the following inspections

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before hydrogenation: Sulfur—1.79 wt. percent, H/C atomic ratio—1.11, gravity—3.6° API, and Conradson carbon content—0.437 wt. percent. 525 s.c.f./bbl. of hydrogen was introduced into the tar to obtain the diluent.

Table I illustrates the surprisingly high conversion obtainable by the hydrogen donor diluent process of this invention as compared to conventional thermal cracking or cracking with only a true diluent. It illustrates the essentiality of partially hydrogenating the thermal tar.

The temperature used during hydrogen donor diluent cracking has been found to be very important, if not critical. It has been found, at least with the heavy diluents here used, that the conversion obtained increases linearly with the temperature of cracking, and this appears to be independent of the diluent/oil ratio. It has also been found, however, that the modified naphtha insolubles (M.N.I.—indicative of the coking propensity of the oil) on total liquid product increase to a maximum and then decrease as conversion increases. The amount of M.N.I. increase at a given conversion increased with the temperature of conversion.

The conclusions from these observations were that at temperatures below about 800° F., the rate of thermal cracking of the oil is faster than the rate of hydrogen donation to the molecular fragments of cracking, which is undesirable; and at temperatures above about 925–940° F., the amount of M.N.I. increase was so great as to result in excessive coking, causing inoperability. For these reasons, the operating temperatures used in this invention are in the range of 800 to 925° F., at least not above 940° F., and preferably 800 to 900° F.

Referring now to Figure 2, a multi-stage operation is disclosed. Feed enters cracking unit 50 by line 51 and diluent by line 52. The mixed feeds are heated preferably to about 800 to 900° F., and the thermal cracking products pass out through line 53 to combine with a recycle in line 54 and enter disengager 55 from which C₃ and lighter gases pass overhead through line 56.

The other cracked products pass through line 57 to fractionator 58 from which C₄ and lighter gases are taken off at 59 and other indicated products at 60, 61, 62 and 63. The 700° F.+ bottoms pass to vacuum still 64 and are separated into a 700 to 900° F. fraction taken off through line 65 to serve as diluent, a heavy gas oil fraction through line 66 and a bottoms fraction through line 67. A portion of the bottoms may be bled off through line 68, the remainder being passed to second stage thermal cracking 69, after blending with diluent from line 70, and is again subjected to HDDC. The total products of second stage cracking pass through line 54 to the disengager 55, fractionator 58 and vacuum still 64, making duplication of these parts unnecessary. They can, of course, be duplicated for the second stage, if desired.

The diluent preferably boiling at 700 to 900° F. is passed through line 65 to a hydrogenation zone 71, a portion being bled off through line 72 when desired. Extraneous thermal tar of similar boiling range may be added through line 73. Hydrogen is added at 74, recovered and recycled by line 75. The hydrogenated diluent is then passed through line 76 to split into two streams in lines 52 and 70, respectively, to supply the separate stages.

In the feed to the second stage, 69, it is preferable to use more diluent than in the first stage. The ratio of bottoms to diluent is preferably between 0.5 and 4.0. The temperature is preferably somewhat higher, e.g. 850 to 925° F. The feed rate may be 0.5 to 3.0 v./v./hr. and a conversion level of 50 to 80% on the bottoms may be obtained for each pass. In the first stage 55 a temperature around 820° F. with feed rates of 1.5 to 5.0 v./v./hr. and pressure of 200 to 1000 p.s.i.g. has been found very satisfactory in tests. With a one to one diluent ratio under these conditions, a conversion of about 45% is obtained. In this multi-stage process it is preferred to keep the conversion level between about

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40 and 60% in the first stage. The reason for this is that the primary purpose of the first cracking stage is to reduce the concentration of paraffinic constituents in the cracking mixture.

EXAMPLE 2

In Table II the hydrogenated thermal tar diluent is compared to lower boiling diluents. The 700–900° F. diluent of this invention is the same as that described for Table I. The 600–700° F. diluent is from the same source as the 700–900° F., but was hydrogenated to a somewhat greater extent as indicated by the available hydrogen. Before hydrogenation, the 600–700 fraction had an H/C ratio of 1.21 and a gravity of 7.6° A.P.I. The tetralin was obtained commercially. The equipment used for these comparative tests comprised a 934 cc. externally heated reactor. The combined feed was continuously charged to the reactor at a rate of 1.7 v./v./hr. The temperature was 820–850° F. and the pressure was about 1000 p.s.i. for the thermal tars, while a pressure of 2000 p.s.i. was necessary to maintain liquid phase conditions with tetralin. The data were correlated and adjusted when necessary to the conversion level indicated.

The feed stock was a 12.9% West Texas residuum having the following inspections: Gravity—7.5° A.P.I., sulfur—3.32 wt. percent, H/C ratio—1.51, and Conradson carbon content—2.4 wt. percent.

Table II

Diluent.....	Tetralin	Tar	Tar (This invention)
Residuum/diluent.....	7.2/1	1/1	1/1
Diluent Boiling Range, ° F.....		600–700	700–900
Cu. Ft. Available H ₂ /bbl. residuum.....	263	425	265
Conversion on residuum, (Vol. percent to 1000° F.—plus coke).....	57.4	43.6	57.4
Coke yield (wt. percent on residuum).....	1.9	0.3	0.1

Several interesting things are illustrated by Table II. When compared at the same available hydrogen and conversion levels to relatively pure compounds such as tetralin as proposed by the prior art, the yield of coke was appreciably lessened. When compared to a lower boiling fraction from the same source as the preferred diluent, using the same diluent/oil ratio, a surprising increase in conversion and decrease in coke yield was obtained, despite the fact that substantially more hydrogen was made available by the 600–700 tar. Table II clearly demonstrates the greater hydrogen transfer efficiency and superiority of the donor diluent over the lower boiling diluents known in the art.

EXAMPLE 3

Table III illustrates the greater efficiency of hydrogen transfer of the diluent of this invention as shown by the ethane/ethylene ratio in the product gases. The conversion was carried out continuously in an externally heated coil. The feed stock was an asphalt obtained from a propane deasphalting operation having the following inspections: Sulfur—4.03 wt. percent, H/C ratio 1.32, gravity—0.7° A.P.I., Conradson carbon—29.4 wt. percent, softening point—189° F., and Modified Naphtha Insolubles (M.N.I.)—17.9 wt. percent. The diluents were again thermal tars derived from clarified oils, having the inspections after hydrogenation, given in Table III. The runs were compared on the basis of the same wt. percent of H₂ from the donor available on combined (asphalt plus donor) feed, and at the same diluent/asphalt ratio,

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Table III

Diluent boiling range, ° F	500-600	700-900
Diluent inspections, after hydrogenation:		
Carbon, wt. percent	87.96	90.24
H/C ratio	1.56	1.25
Gravity, ° A.P.I.	24.7	8.0
Conradson carbon, wt. percent		0.08
Temperature, ° F	870	862
Pressure, p.s.i.g.	400	370
Combined feed rate, v./v./hr.	3.80	3.78
Diluent/asphalt	1/1	1/1
Wt. percent available H ₂ , on combined feed	0.316	0.316
Conversion on asphalt, vol. percent to 1000° F.	48.4	55.2
Products:		
Wt. percent C ₂ H ₄	0.381	0.406
Wt. percent C ₂ H ₆	0.0137	0.00078
Wt. percent Sulfur in 1000° F. +	4.53	3.37
Wt. percent H ₂	0.0177	0.0134
HFS in tot. liq. prod., wt. percent	0.075	0.04
C ₂ H ₆ /C ₂ H ₄	28	520

Table III illustrates that the high boiling hydrogen donors of this invention display an unexpected ability to transfer hydrogen as shown by the great decrease in unsaturates in the products. Note also that with the 700-900 diluent, less free hydrogen appears in the products and better sulfur removal is obtained. Also the hot filtration sediment (HFS) is substantially lower. In vis-breaking operations, HFS is usually the limitation that sets conversion or severity. Any decrease, even slight, in HFS results in appreciable economic gain. Decreasing HFS means higher conversions can be obtained during vis-breaking, without resorting to the use of high quality flux or cut back material to meet HFS specifications.

EXAMPLE 4

A comparative test similar to Example 3 was made, except a different feed stock was used. The feed stock was a 12.9% West Texas residuum, previously described.

A coil arrangement was again used, except for the first column, where the cracking was carried out in a small drum, described in Example 1.

Table IV

Diluent Boiling Range, ° F	Tetralin	430/650	430/650	700/900
Diluent inspections, after hydrogenation:				
Carbon, wt. percent		88.25	88.25	90.24
H/C ratio		1.55	1.55	1.25
Gravity, ° A.P.I.		22.8	22.8	8.0
Conradson Carbon, wt. percent				0.08
Temperature, ° F	835	860	853	820
Pressure, p.s.i.g.	2090	400	380	400
Combined feed rate, v./v./hr.	1.74	4.15	3.59	1.87
Diluent/residuum	1/1	1/1	2/1	2/1
Wt. percent available H ₂ , on combined feed	1.53	0.515	0.344	0.211
Conversion on residuum, Vol. percent to 1000° F.	61.3	50.7	45.2	50
Products:				
Wt. percent C ₂ H ₄	0.517	0.450	0.365	0.627
Wt. percent C ₂ H ₆	0.0049	0.027	0.0069	<0.0015
Wt. percent H ₂	0.0475		0.016	0.012
C ₂ H ₆ /C ₂ H ₄	106	17	53	>450

The comparisons of the C₂H₆/C₂H₄ ratios in Table IV again illustrate the surprising increase in the transference of hydrogen when using the high boiling diluent proposed by this invention.

EXAMPLE 5

Table V illustrates the efficiency of a non-thermal tar hydrogen donor diluent, hydrogenated clarified oil extract, prepared according to this invention. The table also presents a control run without a diluent to evaluate the effect of the donors on M.N.I. The feed was a 29%

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Hawkins residuum, similar to that given in Table III. The extract, before hydrogenation, had an A.P.I. gravity of 1.6°, and an H/C ratio of 1.13. The equipment used was the cracking coil previously described.

Table V

29% Hawkins Residuum	66.6	66.6	100
Hydrog. 700/900° F. Thermal Tar ¹	33.4		
Hydrog. Clarified Oil Extract ²		33.4	
Temperature, ° F	830	820	820
Pressure, p.s.i.g.	420	400	400
Feed Rate, v./v./hr. in coil	3.38	3.76	3.60
Yields, Wt. percent on Resid.:			
Conversion to 1000° F.	49.0	38.6	37.9
C ₃	2.6	0.84	1.58
C ₄ -430° F	12.2	21.4	11.0
430-650° F	12.4		
430-1000° F		60.6	22.2
650-1000° F	724		
1000° F. +	51.0	61.4	62.1
Wt. Percent Change in Mod. Naphtha Insoluble ³	+8.6	-0.6	+37.3

¹ Obtained from thermal cracking clarified oil; hydrogenation took up 400 s.c.f. H₂/bbl.,—same diluent as described in Table III.

² Phenol extract of clarified oil; hydrogenation took up 600 s.c.f. H₂/bbl.

³ Calculated on residuum from the M.N.I. in the total liquid product.

While the thermal tar was better than the extract, considering the difference in conversion levels, both diluents prevented polymerization of the cracked products to naphtha insolubles, whereas visbreaking resulted in a major increase in M.N.I. as shown in the third column. It is well known in the art that M.N.I. increases very rapidly with increasing conversion during cracking so that at 49% conversion to 1000° F.—, visbreaking would have resulted in an M.N.I. increase well over 60%.

EXAMPLE 6

The next table illustrates the surprising results obtained by only partially hydrogenating the diluent. The feed stock had the following inspections: 84.87 wt. percent carbon, 1.39 H/C ratio, 3.8° A.P.I. gravity, 24.6 wt. percent Conradson carbon, 17.4 wt. percent M.N.I., and 155° F. softening point.

Table VI

Temperature, ° F	820	820	820	820	850
Feed rate (Coil), v./v./hr.	3.60	3.62	3.76	3.42	4.30
Pressure, p.s.i.g.	400	400	400	400	360
Resid. Conversion to 1000° F., wt. percent	37.9	40.5	38.6	43.3	43.7
Residuum	(1)	(1)	(1)	(1)	(1)
Diluent	None	(2)	(2)	(2)	E. Texas Gas Oil ³
Wt. Percent Diluent in Feed	0	33.4	33.4	33.4	50
Cu. ft. H ₂ Added to Diluent		400	600	800	(4)
Modified Naphtha Insolubles ⁵	23.9	19.9	17.3	17.9	19.7

¹ 27% Hawkins.

² Clarified Oil Extract.

³ East Texas Virgin gas oil (500-750° F.)

⁴ The virgin gas oil is highly saturated (H/C=1.85) compared with a hydrogenated clarified oil extract (H/C=1.25). Directionally this is similar to the use of an exhaustively hydrogenated clarified oil which would have required 3650 cu. ft. H₂/bbl. in order to reach 1.85 H/C atomic ratio in the hydrogenated product.

⁵ Calculated on residuum (starting M.N.I.=17.4)

Table VI shows that there is an optimum level of partial hydrogenation. When going from a state of no diluent hydrogenation to one of substantially complete hydrogenation, diluent efficiency reaches a peak, as indicated by a minimum M.N.I. content (17.3), and then declines.

EXAMPLE 7

Table VII illustrates the applicability of this invention to various feed stocks. Note in the runs where diluent was used, the substantial reduction in coke yields compared with non-diluent visbreaking runs.

Table VII

Feed Stock.....	12.9% West Texas Resid.		27% Hawk-ins Resid.	Hawk-ins Asphalt	900° F.+ Bachaquero Resid.	Coleville Crude		Clarified Oil	16% West Texas Residuum
Inspections:									
Carbon, wt. percent.....	85.28		84.87	83.95	84.1	85.14		85.33.....	87.58.
Sulfur, wt. percent.....	3.32		4.54	4.03	3.36	3.43		1.32.....	2.60.
H/C atomic ratio.....	1.51		1.39	1.32	1.47	1.57		1.53.....	1.27.
Gravity, °A.P.I.....	7.5		3.8	-0.7	5.7	13.6		10.8.....	9.5.
Conradson carbon, wt. percent.....	21.4		24.6	29.4	20.3	11.6		15.7.....	
M.N.I., wt. percent.....			22.8	1	13.2	8.8			
Softening point, °F.....	134		155		115.5				
Diluent, 700/900° F.:									
Thermal Tar, wt. percent.....	None	33.4	50	50	20	10	None	Thermal tar, ¹	Clarified oil, ²
Diluent Hydrogenation, cubic feet H ₂ /bbl.		400	400	400	550	820		500.....	438.
Temperature, °F.....	815-860	820	853	862	798	840-850	830-850	860.....	
Pressure, p.s.i.g.....	1500	400	380	370	400	390	510	400-1100.....	
Feed rate, v./hr./v.....	3.44	1.87	3.56	3.78	1.21	2.13	2.03		
Unit.....	Drum	Coil	Coil	Coil	Coil	Drum	Drum	Batch (300 c.c.).	Batch (300 c.c.).
Conversion to 1000° F.—, Vol. percent on Resid.	30	50	53.2	55.2	36	70.6	72.2	27.....	42.
Yields, Wt. percent on Feed:									
Coke.....	2.5	0.8	0.05	0	0.19	0.14	1.8	<0.1.....	2.5.
C ₃ —Gas.....	1.3	2.9	1.8	1.8	2.8	0.76	3.2	1.6.....	3.3.

¹ 700° F.+ from thermally cracked clarified oil.² Diluent Inspections: H/C 1.36; S. 1.66 wt. percent.³ 900° F.+.⁴ 55.8 vol. percent on 1000° F.+ in Coleville Crude.⁵ 650° F.—.

EXAMPLE 8

This example illustrates HDDC with recycle of the diluent. The cracking was carried out in a coil. The products separation, diluent hydrogenation and diluent blending with feed were carried out batch-wise. This was done for six cycles and equilibrium conditions were closely approached. The diluent and feed stock have been described in the previous examples.

Table VIII

Feed composition, wt. percent:	
12.9% West Texas residuum	34.0
1000° F.+ recycle bottoms	32.7
700-900° F. recycle diluent	26.5
Fresh 700-900° F. thermal tar (blended with spent diluent, and hydrogenated therewith)	6.8
Diluent hydrogenation (includes fresh tar):	
Temperature, ° F.....	700
Pressure, p.s.i.g.....	500
Feed rate, v./v./hr.....	0.5
Catalyst	Molybdenum sulfide
H ₂ consumption, s.c.f. H ₂ /bbl. of diluent.....	400
Cracking conditions (coil operation):	
Temperature, ° F.....	820
Pressure, p.s.i.g.....	400
Feed rate, v./v./hr.....	2
Products, based on fresh residuum and make-up tar:	
Coke, wt. percent	1.8
C ₃ —, wt. percent	7.6
C ₄ , vol. percent	3.7
C ₅ —430° F., vol. percent	38.7
430-700° F., vol. percent	41.7
700-900° F.....	0
900-1000° F., vol. percent	14.9
1000° F.+, vol. percent	1.8

It will be appreciated by those skilled in the art that when diluent recycle operation is practiced, the constituents in the recycled diluent such as paraffins that do not contribute to hydrogen donation can be removed, if necessary, by treating all or part of the recycled diluent by solvent extraction, thermal cracking or catalytic aromatization.

Having described this invention and presented specific examples thereof, what is sought to be protected by Letters Patent is succinctly set forth in the following claims.

30 What is claimed is:

1. The process of upgrading heavy residual hydrocarbons to lighter products which comprises blending 0.25 to 4 parts by volume of a diluent, obtained as stated hereinafter, with one volume of the feed, thermally cracking in a first stage the feed-diluent mixture by heating to 800 to 900° F. under a pressure of not more than 1000 p.s.i.g. and for a residence time of 0.25 to 5 hours, separating lighter products from a 700° F.+ bottoms fraction of the cracked mixture, separating the bottoms fraction into a 700 to 900° F. cut containing a minimum aromatic content of 40 wt. percent and a heavier fraction, partially hydrogenating the 700 to 900° F. cut under pressure in the presence of a hydrogenation catalyst by adding thereto 200 to 1000 s.c.f. of hydrogen to obtain a hydrogen/carbon atomic ratio in the range of 0.7 to 1.6, passing the heavier fraction from the bottoms to a second stage thermal cracking zone, blending 0.5 to 4 parts by volume of diluent therewith, and thermally cracking the mixture under pressure at a temperature of 850 to 925° F., and recycling the partially hydrogenated 700 to 900° F. cut to both cracking stages to serve as said diluent.

2. Process according to claim 1 wherein the second stage cracking is carried out at more severe conditions than the first.

3. In a conversion process wherein a heavy petroleum oil is admixed with a hydrogen donor diluent and subjected to conditions of non-catalytic, liquid phase hydrogen donor diluent cracking in the absence of extraneous hydrogen at a temperature in the range of 800° to 925° F. the improvement which comprises utilizing as the hydrogen donor diluent a partially hydrogenated aromatic naphthenic containing thermal tar, said tar having been obtained by first extensively thermal cracking a cracked, low value, high boiling refinery material, segregating and recovering therefrom a bottoms tar fraction having a minimum boiling point of 700° F. and a minimum aromatic content of 40 wt. percent and hydrogenating the tar fraction with from 200 to 1000 s.c.f. hydrogen/barrel to obtain a H/C atomic ratio of 0.7 to 1.6.

4. The process of claim 3 wherein the precursor of said hydrogen donor diluent comprises a catalytically cracked oil having an A.P.I. gravity below 20°.

5. The process of claim 3 wherein said process com-

prises a vis-breaking type of operation producing residual fuel oils.

6. A process according to claim 3 wherein following the hydrogen donor diluent cracking step the spent hydrogen donor diluent is separated from the cracked products and partially hydrogenated to introduce about 1 to 3 hydrogen molecules into the aromatic-naphthenic donor molecule while leaving one or more aromatic rings in the molecule unhydrogenated and at least a major part thereof is recycled to the hydrogen donor diluent step for cracking additional heavy petroleum oil.

7. A process according to claim 3 wherein following the hydrogen donor diluent cracking step the spent donor diluent is separated from the cracked products and partially hydrogenated and the partially hydrogenated hydrogen donor diluent recycled to the hydrogen donor diluent cracking step.

8. A hydrogen donor diluent cracking process which comprises admixing a heavy hydrocarbon oil with 25% to 400% by volume of a hydrogen donor diluent containing a predominate proportion of condensed ring aromatic-naphthenic compounds and having a boiling point above about 700° F., having a minimum aromatic content of about 40% by weight, and made by only partially hydrogenating a cracked high boiling refinery material with from about 200 to 1000 s.c.f. of hydrogen per barrel of feed to obtain a hydrogen donor diluent having a H/C atomic ratio between about 0.7 and 1.6, thermally cracking the mixture under hydrogen donor diluent non-catalytic cracking conditions whereby said hydrocarbon oil feed is pyrolytically converted and said hydrogen donor diluent transfers hydrogen to the products of the pyrolysis, said hydrogen donor diluent cracking conditions including a temperature in the range of 800° F. to 925° F., and a pressure sufficient to maintain substantially liquid phase conditions, separating the thermally cracked mixture to obtain product lower boiling hydrocarbon fractions, spent donor diluent and bottoms, only partially hydrogenating at least a major portion of said spent donor diluent by introducing into said donor diluent 200 to 800 s.c.f. of H₂ bbl. of spent donor diluent, and recycling the partially hydrogenated donor diluent to form at least a portion of said hydrogen donor diluent admixed with said heavy hydrocarbon oil feed.

9. A process according to claim 8 wherein the hydrogen donor diluent is produced by partially hydrogenating a thermal tar produced by cracking catalytic cycle stock.

10. The process of claim 11 wherein said make-up consists of thermal tar obtained by thermally cracking a catalytic cracking cycle stock.

11. A process according to claim 8 wherein a minor amount of said spent hydrogen donor diluent fraction is bled from said process and replaced by make-up hydrogen donor diluent precursor whereby the effective hydrogen transfer characteristics of said hydrogen donor diluent fraction are maintained, said make-up hydrogen donor diluent precursor comprising a thermal tar obtained from cracking a cracked, low value hydrocarbon oil and having a boiling point above about 700° F. and containing a major portion of polycyclic condensed ring aromatic-naphthenic compounds and in which the added precursor is only partially hydrogenated during said partial hydrogenation step to obtain a hydrogen donor diluent having at least one aromatic ring in the molecule which is unhydrogenated and having a H/C atomic ratio of about 0.7 to 1.6.

12. A hydrogen donor diluent cracking process which comprises admixing a heavy hydrocarbon oil with 25% to 400% by volume of a hydrogen donor diluent containing a predominate proportion of condensed ring aromatic-naphthenic compounds and having a boiling point above about 700° F., having a minimum aromatic content of about 40% by weight, and made by only partially hydrogenating a cracked low value high boiling refinery material with from about 200 to 1000 s.c.f. of hydrogen

per barrel of said refinery material to obtain a hydrogen donor diluent having a H/C atomic ratio of about 0.7 to 1.6, thermally cracking the mixture under hydrogen donor diluent non-catalytic cracking conditions whereby said hydrocarbon oil feed is pyrolytically converted and said hydrogen donor diluent transfers hydrogen to the products of cracking, said hydrogen donor diluent cracking conditions including a temperature in the range between about 800° F. and 925° F., and a pressure sufficient to maintain substantially liquid phase conditions, and separating the thermally cracked mixture to obtain product lower boiling hydrocarbon fractions, spent donor diluent and bottoms.

13. In a petroleum oil thermal cracking process wherein a hydrocarbon oil is subjected to pyrolysis to produce lower boiling hydrocarbons, the improved method for cracking such hydrocarbon oil while substantially inhibiting coke formation and deposition which comprises admixing with said hydrocarbon oil 0.25 to 4 volumes of hydrogen donor diluent per volume of oil, said hydrogen donor diluent comprising a major proportion of condensed naphthenic-aromatic ring compounds obtained as a fraction boiling between about 700° and 900° F. by only partially hydrogenating a high boiling thermally cracked tar boiling above about 700° F. to produce condensed ring aromatic-naphthenic compounds in which at least one aromatic ring in the molecule remains unhydrogenated and the hydrogen donor diluent has a H/C atomic ratio of between about 0.7 and 1.6, thermally cracking the mixture, recovering from the mixture of cracked products spent hydrogen donor diluent, only partially hydrogenating at least a major portion of the recovered spent donor diluent fraction and recycling the partially hydrogenated donor diluent to convert further amounts of said hydrocarbon oil feed.

14. A thermal cracking process which comprises admixing a heavy high boiling hydrocarbon oil with 25 to 400% by volume of a hydrogen donor diluent having a boiling range above about 700° F. and made by only partially hydrogenating a thermally cracked catalytic cycle oil with 200 to 1000 s.c.f. of hydrogen per barrel of said cycle oil to obtain a hydrogen donor diluent having a H/C atomic ratio between about 0.7 and 1.6 and a minimum aromatic ring content of 40 wt. percent, thermally cracking the admixture under hydrogen donor diluent non-catalytic cracking conditions to convert the heavy hydrocarbon oil to lower boiling products and so that the hydrogen donor diluent transfers hydrogen to the converted products, said cracking conditions including a temperature between about 800° F. and 925° F. and a pressure sufficient to maintain substantially liquid phase conditions, and recovering lower boiling hydrocarbons from the converted products.

15. A thermal cracking process which comprises admixing a heavy high boiling hydrocarbon oil with about 25 to 400% by volume of a hydrogen donor diluent having a boiling range between about 700° F. and 900° F. and made by only partially hydrogenating a thermal tar obtained by extensively thermally cracking a cracked, low value, high boiling refinery material and segregating a tar fraction therefrom having a minimum boiling point of about 700° F., said hydrogen donor diluent comprising a partially hydrogenated condensed ring aromatic-naphthenic containing thermal tar having a minimum aromatic content of about 40% by weight and being only partially hydrogenated with from 200 to 1000 s.c.f. of hydrogen per barrel of feed to obtain a hydrogen donor diluent having a H/C atomic ratio of between about 0.7 and 1.6, then thermally cracking the admixture under hydrogen donor diluent non-catalytic cracking conditions to convert the heavy high boiling hydrocarbon oil to lower boiling products and so that the hydrogen donor diluent transfers hydrogen to the converted products, said cracking conditions including a temperature between about 800° F. and 925° F. and a pressure sufficient to

maintain substantially liquid phase conditions, and recovering lower boiling hydrocarbons from the converted products.

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