Nov. 4, 1958 C. B. HERMAN 2,859,169

HEAVY OIL CONVERSION PROCESS

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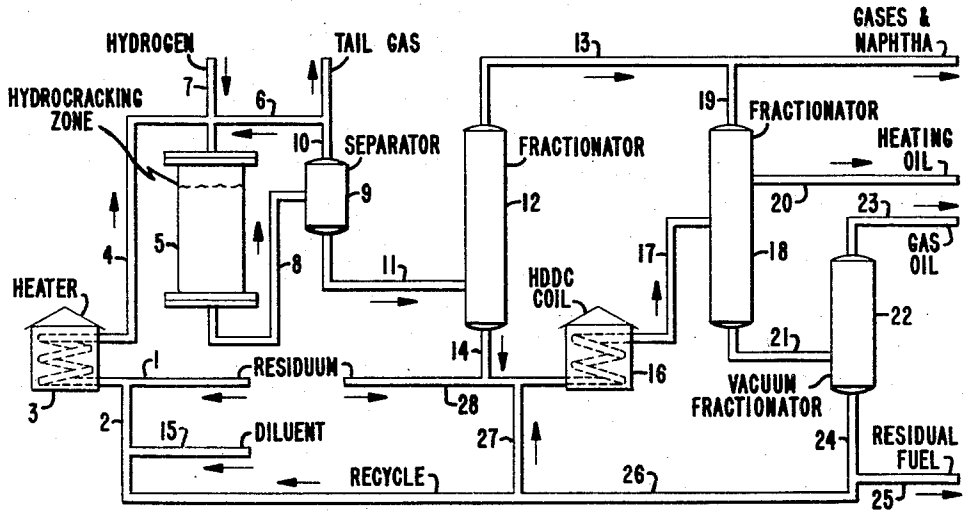


FIGURE I

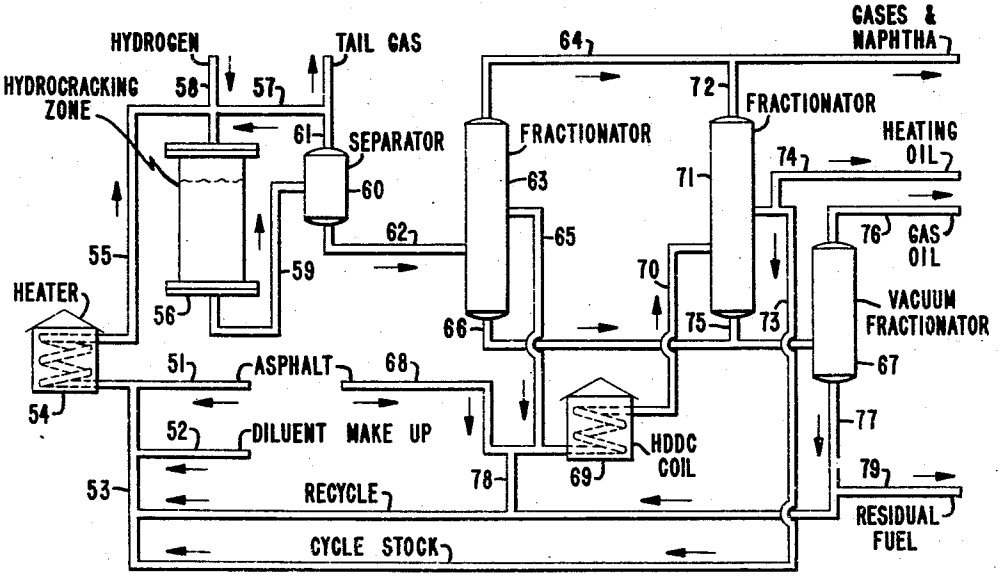


FIGURE II

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HEAVY OIL CONVERSION PROCESS

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3 Claims. (Cl. 208—59)

The present invention relates to the conversion of heavy hydrocarbons. The invention is more particularly concerned with a process for producing naphthas of motor fuel quality and gas oils of catalytically cracking quality from heavy oils such as asphalts and vacuum residua. This invention proposes a combination heavy oil conversion process comprising the steps of catalysis and hydrogenolysis.

In brief compass, the present invention comprises a heavy oil conversion process wherein a heavy oil is converted in the presence of a diluent oil. The diluent oil is aromatic-naphthenic in nature, and upon hydrogenation displays good hydrogen donor properties. A mixture of a heavy oil and a diluent oil is subjected to hydrocracking conditions in the presence of a hydrogenation catalyst and in the presence of free hydrogen. The products from the hydrocracking are separated to obtain a fraction containing the diluent oil, now partially hydrogenated, and this fraction is mixed with additional amounts of the heavy oil. This second mixture is then thermally treated under hydrogen donor cracking conditions to obtain further conversion of the oil with transfer of hydrogen from the hydrogenated diluent oil to the conversion products.

Succinctly, this invention comprises the essential steps of hydrocracking a heavy oil feed stock while the feed stock is diluted with a highly aromatic oil to obtain conversion products and a hydrogen donor diluent. The hydrogen donor diluent is then used to convert further amounts of the feed stock in the absence of a catalyst and free hydrogen.

It recently has been discovered that it is practicable to convert heavy hydrocarbon materials such as petroleum residua by directly hydrogenating the material using a hydrogenation catalyst. In such a process, conditions are adjusted to obtain cracking of the hydrocarbon feed with introduction of hydrogen into the fragment molecules formed by the cracking. Thus high boiling, normally valueless hydrocarbonaceous materials are converted into lower boiling products having a much higher value. Because this high boiling heavy material is usually extremely deleterious to catalyst and has a high propensity to deposit coke on catalyst, care must be used in this type of catalytic upgrading process. Despite this operating drawback of catalyst deterioration, this process is gaining favor. Not only are increased amounts of valuable products obtained from normally waste materials, but the products obtained are of high quality. This hydrocracking process substantially desulfurizes the material treated and does not yield any substantial amount of unsaturated or unstable products.

An alternative method of upgrading heavy oils, termed hydrogen donor diluent cracking (HDDC), has also been proposed. In this method the hydrogen is introduced into the oil being converted by a hydrogen carrier material in the absence of catalyst. In this HDDC process, a hydrogen donor diluent material, aromatic-naphthenic in nature, is especially prepared by partial hydrogenation

and is admixed with the oil to be converted. The resulting mixture is then thermally treated such that the oil is cracked and hydrogen is transferred from the donor diluent to the cracked products. In this manner of hydrocracking oils, the oil being upgraded is not contacted directly with a hydrogenation catalyst and does not impair catalyst activity by contamination. This proposed HDDC process has disadvantages in that a special hydrogenation zone is required for preparation of the diluent and that little desulfurization of the oil occurs.

The present invention proposes an integration of the two above-described hydrocracking processes. The inherent disadvantages of each process are greatly minimized through this integration and yet their advantages of being able to upgrade difficult to convert oils are retained. By means of this combination process, heavy oils can be converted to optimum yields of catalytic cracking quality gas oils and high quality naphthas or gasolines. The relative proportion of gas oils and gasolines may be varied as demanded by economic considerations.

In light of the above, it is an object of this invention to propound a combination process for upgrading heavy low value oils. It is another object of this invention to present to the art a conversion process comprising the steps of hydrocracking an oil diluted with a hydrogen donor precursor in the presence of hydrogenation catalyst to obtain lighter conversion products and a hydrogen donor diluent, and then using the hydrogen donor diluent, or a mixture of the diluent and some or all of the heavier products from the hydrocracking process, to convert further amounts of the oil in a hydrogen donor diluent cracking zone.

These and other objects and advantages will become more clear as this description proceeds during which the attached drawings, forming a part of this specification, are described in detail. The drawings are presented by way of illustration only and the invention is not to be limited thereby.

Figure I of the attached drawing depicts the two-step conversion process of the present invention wherein the hydrogen donor diluent material is utilized on a once through basis.

Figure II of the drawing depicts this two-step process when recycle operation is practiced as to the hydrogen donor diluent material.

The heavy oil which forms the principal charging stock for the present invention is preferably a hydrogen deficient petroleum derived oil such as a heavy crude oil or a residual fraction therefrom. Particularly preferred is a heavy oil characterized by an API gravity of —5° to 20°, a Conradson carbon of 5 to 50 wt. percent and an initial boiling point above about 850° to 1100° F. This invention is, however, capable of enjoying broader applications. Thus heavy oils such as coal tars, shale oils, natural tars and asphalts, cycle stocks, aromatic extracts, etc. may conveniently be processed.

The hydrogen donor diluent precursor used in this invention is composed of predominantly proportions of aromatic-naphthenic molecules, or partially condensed ring structures, having the ability to readily take up hydrogen in a hydrogenation zone and to release it in a themal cracking zone. Aromatic-naphthenic molecules are molecules having a few, say one or two, aromatic nuclei with attached naphthenic or partially hydrogenated ring structures. Tetralin is an example of a hydrogen donor type molecule. Totally condensed ring structures such as benzene or fully hydrogenated ring structures such as cyclo-hexane do not display hydrogen donor properties of the type contemplated. The aromatic-naphthenic ring structures are refractory and will pass through

a thermal cracking zone relatively unaltered. These structures are, therefore, susceptible to being recovered from reaction mixtures and being regenerated by partial hydrogenation. Some loss of the diluent material will, however, be experienced.

In particular, it has been found that the thermal tars obtained by the thermal cracking of catalytic cycle stocks contain excellent hydrogen donor type molecules. It has also been found, however, that lube oil extracts, virgin gas oils, extracts of catalytic cycle stocks and clarified oils, or the cycle stocks and clarified oils themselves, and cycle oils and heavier products from high temperature, low pressure thermal cracking operations can serve as sources of the donor diluent.

The catalyst that is used in the first hydrocracking stage of this invention is preferably a sulfur resistant hydrogenation catalyst such as cobalt molybdate, nickel tungsten sulfide and many other catalyst of this nature which are not deactivated by contact with sulfur contaminating materials. The cobalt molybdate catalyst may actually be mixtures of cobalt, molybdenum, and other selected metals. These catalysts can be supported on suitable carriers such as alumina, kieselguhr, charcoal, silica gel, celite, etc. and may have certain compounds added to them to improve their properties. The catalyst is preferably used as a fixed bed composed of catalyst particles of a size in the range of 10 to 80 mesh.

The catalyst may be suitably activated or treated prior to use. With cobalt molybdate supported on alumina this treatment may comprise heating the catalyst to about 1400° F. for a time of about 6 to 48 hours followed with washing with gas oil.

The catalyst may be suitably regenerated by means known by the art. For example, the catalyst can be regenerated by treatment with an oxygen containing gas to turn off coke-like deposits. Two or more catalytic reactors may be used in this invention to permit continuous operation of the process while allowing regeneration of the catalyst. Alternatively, a fluidized catalyst operation can be used with one vessel for carrying out the reaction and one for catalyst regeneration.

The activity of the catalyst may be increased during use without severe oxidation regeneration treatment by discontinuing the flow of the heavy oil to the catalyst chamber and allowing the diluent to wash over the catalyst to remove, at least in part, some of the carton and metal contaminant deposits.

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

Referring now to Figure I, the heavy oil to be upgraded, e. g., a vacuum residuum in line **1**, is admixed with a hydrogen donor diluent precursor supplied via lines **15** and **2**. Certain recycle streams may also be added at this point as will hereinafter appear. The resulting mixture is heated in heater **3**, which may be a conventional furnace, to the necessary conversion temperature and then is passed by line **4** to the hydrocracking zone **5**. Hydrogen containing gas is admitted to the contents of line **4** by line **6**. Makeup hydrogen may be supplied by line **7**. This hydrogen gas may be suitably preheated, if desired. The hydrogen containing gas has preferably a purity of over 70%. After passing through the hydrocracking zone, the mixture is transferred by line **8** to a separator **9** wherein the spent hydrogenation gas is removed. This spent gas is removed by line **10** from the separator and a portion of it may be bled from the process, and the remainder transferred to the hydrocracking zone by line **6**.

After this separation, the cracked mixture is transferred by line **11** to a conventional fractionator **12**. The cracked mixture may be divided into as many fractions as desired at this point. As shown, however, only material boiling in the naphtha range and lighter, e. g., below 430° F., is removed and transferred by line **13** to further conventional separating and finishing processes. The remainder of the material in this example is transferred by line **14** to the HDDC unit. It is to be pointed out, however, that a diluent fraction only can be recovered at this point and transferred to the HDDC unit.

The original diluent supplied to the process by line **15** is selected to be of a boiling range different from that of the residuum. Preferably, the lowest boiling range of diluent is used that will still sufficiently solubilize with the heavy oil feed. It is preferred to use diluents boiling in the range within the limits of 400° to 650° F., although diluents of higher boiling range up to about 1,000° F. can readily be used. If a diluent of a 430° to 650° F. boiling range is used, then in order to recover this diluent in fractionator **12**, the material transferred by line **14** has a boiling point at least as low as 430° F.

The hydrogen donor material in line **14** which, in this case illustrated, also comprises the heavy bottoms from the hydrocracking zone, is admixed with additional amounts of residuum supplied by line **28**. Preferably the hydrogen donor material and heavy bottoms in line **14** are admixed with ½ to 1 vols. of residuum. In normal operation, about 25 to 50% of the heavy oil or residuum feed to the process will be processed in the hydrocracking zone **5** and the remainder will be treated in the HDDC unit **16**. Additional recycle streams may be mixed with the feed to the HDDC unit if desired, as will hereinafter appear.

The residium diluted with the hydrogen donor diluent material is then subjected to hydrogen donor diluent cracking conditions. Any conventional means may be used to accomplish this. As shown, a heating coil **16** is used to bring the materials to reaction temperatures. A coil and drum arrangement may be used if desired. This will effect long time, low temperature cracking conditions thus affording a more complete hydrogenation of cracked products. The thermally treated mixture is then transferred by line **16** to a conventional fractionation zone **18**. The thermally treated mixture may be separated into several fractions, if desired, at this point. As shown, products boiling in the naphtha range and lighter are removed by line **19** and combined with the contents of line **13**. Heating oils boiling in the range above naphtha up to about 650° to 700° F. are removed by line **20** as product. These heating oils may conveniently be subjected to further processing such as severe hydrocracking or catalytic cracking to obtain further amounts of naphthas of gasoline quality or used as flux for residual fuels. The bottoms from the separation are transferred by line **21** to a conventional vacuum distillation unit **22** wherein gas oils boiling up to about 950° to 1100° F. are removed by line **23**. These gas oils may also be catalytically cracked or can be used as a flux in residual fuels.

The bottoms from this separation are removed by line **24**. It is desirable to remove a portion of these bottoms by line **25** to prevent undue buildup of extremely refractory constituents and catalyst contaminants in the system. Preferably, for the process illustrated, approximately 5 to 50% of these bottoms will be bled from the process when a cut point of 1,000° F. is used. The remainder of the bottoms is recycled to the hydrocracking zone via line **26** and/or the HDDC zone via lines **26** and **27**. Preferably all of the bottoms are recycled to the HDDC unit **16**, as they are not amenable to further catalytic conversion and will cause more rapid catalyst contamination.

For the process above described, it is preferred to obtain conversion in the hydrocracking zone based on fresh residuum feed in the range of about 30 to 50 vol. percent to 1050° F. and lighter products. This is somewhat milder than is customarily used. However, this mild conversion greatly promotes catalyst life and the selectivity of the hydrocracking step. Conversions in the range of 50 to 80 vol. percent to 1050° F. and

lighter products, based on fresh residuum feed, are preferably obtained in the HDDC unit.

These conversion ranges are preferred when it is desired to substantially completely convert the residuum. However, the process may be operated more in the nature of a vis-breaking process so as to produce substantial amounts of residual fuel as demanded by market conditions. If a vis-breaking type operation is practiced, then the contents of line **24** will not be recycled. When residual fuel is produced, a portion of the heating oil in line **20** is preferably used to flux the residual oil with gas oil in line **23** still being charged to catalytic cracking.

For the process as described with reference to Figure I, the operating conditions are summarized in Table I. This table also presents a specific example of operating conditions. Table II presents the products obtainable from the feed stocks indicated when the process is operated in accordance with example of Table I.

Table I

	Range	Example
Hydrocracking zone:		
Pressure, p. s. i. g.	0 to 1,000	400.
Temperature, °F	700 to 850	780.
Space velocity, v./v./hr.	0.2 to 2	0.5.
Diluent/heavy oil ratio, vol./vol.	3/1 to 1/2	2/1.
Diluent boiling range, °F.	Within 400 to 1,000.	430 to 650.
Hydrogen rate, s. c. f./bbl. mixture.	200 to 500	200 (consumption).
	300 to 1,000	900 (charge).
1,050° F.—Conversion,[2] vol. percent.	30 to 60	50.
Catalyst	Sulfur Resistance Hydrogenation Catalyst.	Cobalt Molybdate.
HDDC Zone:		
Pressure, p. s. i. g.	0 to 1,000	400.
Temperature, °F	700 to 900	805.
Throughput, v./v./hr.	0.5 to 5	1.
Diluent/heavy oil [1] ratio, vol./vol.	1/1 to 1/3	1/2.
Diluent boiling range, °F.	Within 400 to 1,000.	430 to 650.
1,050° F.—Conversion,[2] vol. percent.	40 to 90	60.

[1] Including any recycle streams.
[2] 1,050° F. conversion is defined as 100 vol. percent fresh heavy oil feed and diluent less vol. percent of products boiling above 1,050° F.

Table II

Feed Inspections	Heavy Oil—Vacuum Residuum	Diluent—Aromatic Extracts
Elemental Analysis, Wt. percent:		
Carbon	87.0	89.7
Hydrogen	11.0	8.4
Sulfur	2.0	1.34
Nitrogen and Oxygen		0.56
H/C atomic ratio	1.5	1.12
Gravity, °API	10.0	1.9
Conradson carbon, Wt. percent	20	6.5
Ash at 800° C., Wt. percent	0.20	Trace
Initial boiling point, °F.	900	459
Final boiling point, °F.		950
Aromatics		85%
Yields—Percent on Residuum and diluent:		
C_3-gas, Wt. percent		1.8
C_4 Vol. percent		1.5
C_5—430° F. Vol. percent naphtha		11.4
430°–650° F., Vol. percent heating oil		15.4
650°–1,000° F., Vol. percent gas oil		48.7
1,000° F+residual fuel		21.2

With reference to Figure II, a process will be described wherein recycle operation as to the diluent precursor is practiced. The process is illustrated as requiring makeup diluent, but it has been found that with many feed stocks there will be a sufficient amount of aromatic-naphthenes in the feed, or materials that will reduce the aromatic-naphthenes to fully meet the diluent requirements of the process, particularly if the naphtha product is undercut to about 375° F. In some instances, an excess of diluent will be produced. For example, it has been found that a large amount of naphthalene will be produced by the process in some cases.

In this example an asphalt feed is supplied to the process by line **51** and is mixed with diluent makeup material, from the sources previously indicated, supplied by line **52** and with various recycle streams supplied by line **53**. The resulting mixture is then heated to reaction temperatures in heater **54** and transferred to a fixed bed hydrocracking zone **56** by line **55**. Hydrogen is mixed with the heated mixture via line **57**, makeup hydrogen being supplied to the process by line **58**. After being subjected to hydrocracking, the mixture is transferred to separator **60** via line **59** wherein the spent hydrogen gas or tail gas is removed by line **61**. The mixture is then transferred from the separator by line **62** to a fractionator **63** wherein products boiling below 430° F. are separated and removed by line **64**. In this case a diluent fraction boiling in the range of about 430° to 700° F. is separated and removed by line **65**. The remaining bottoms are transferred by line **66** to vacuum distillation unit **67**. The hydrogen donor diluent fraction in line **65** is admixed with additional amounts of fresh asphalt supplied by line **68** and transferred to the thermal cracking or HDDC unit **69**. After being thermally treated, the mixture is passed via line **70** to a fractionator **71**. Again naphthas and light gases are separated and removed by line **72** and mixed with the contents of line **64** and sent to further conventional processing.

A fraction boiling in the diluent range is separated and transferred by lines **73** and **53** to the hydrocracking unit. This fraction contains a substantial proportion of the original diluent precursor introduced into the process because, as previously explained, these molecules are relatively refractory and will pass through the process without substantial alteration. However, material not displaying hydrogen donor properties such as paraffins are cracked into the diluent boiling range and it is desirable to remove or bleed from the process a portion of this diluent fraction by line **74** as heating oil product. The makeup diluent supplied to the process by line **52** will make up this loss plus the small loss of diluent caused by cracking of the diluent molecules.

The bottoms from fractionator **71** boiling above about 700° F. are transferred via lines **75** and **66** to a vacuum fractionator **67**. The combined bottoms from fractionators **63** and **71** have removed therefrom in the vacuum fractionator gas oils boiling up to about 1000° F. These gas oils are removed from the process via line **76**. The bottoms from the vacuum unit are transferred by lines **77** and **53** to the hydrocracking unit and/or by lines **77** and **78** to the HDDC unit. As previously described, it is desirable to bleed up to about 5 to 50% of this bottoms fraction from the process by line **79** as a residual fuel product. If it is desired to operate the process under milder conversion conditions, a substantial amount of residual fuel product may be withdrawn via line **79** and the bottoms recycle operation eliminated.

Instead of bleeding via line **74** some of the diluent fraction from the process in order to maintain its effective aromaticity, other means may be used to concentrate the aromatic-naphthenes or aromatic ring structures in this fraction. For example, the contents of line **73** may be subjected to an extraction process such as phenol, furfurol, or sulfur dioxide extraction to concentrate the aromatics therein, and the raffinate from the extraction process can be withdrawn from the process. Alternatively, the contents of line **73** may be subjected to an aromatization process to increase the aromatic content or can be subjected to mild thermal cracking to remove therefrom paraffins and alkyl groups that do not contribute to the hydrogen donor characteristics of the fractions.

Various modifications of this invention will be readily apparent to those skilled in the art. What is sought to be protected by Letters Patent is succinctly set forth in the following claims.

What is claimed is:

1. A heavy oil conversion process which comprises forming a mixture of a heavy oil with a diluent oil suitable for being converted to a hydrogen donor diluent and comprising major proportions of aromatic-naphthenes, hydrocracking the mixture in the presence of a hydrogenation catalyst and in the presence of hydrogen under hydrocracking conditions to obtain a 1050° F.— conversion in the range of 30 to 60%, separating the cracked mixture to obtain a fraction boiling above 400° F. containing said diluent oil now partially hydrogenated, admixing the fraction so separated with additional amounts of said heavy oil, thermally treating the resulting mixture under hydrogen donor diluent cracking conditions to obtain a 1050° F.— conversion in the range of 40 to 90%, and separating the thermally treated mixture.

2. A hydrocarbon conversion process which comprises mixing with a heavy oil ½ to 3 vols of a diluent oil comprising major proportions of aromatic-naphthenes boiling in a range within the limits of 400° and 1000° F. to form a first mixture, adding to said first mixture 300 to 1000 s. c. f. of a free-hydrogen containing gas per vol. of mixture and passing the mixture over a hydrogenation catalyst under hydrocracking conditions, said hydrocracking conditions including a temperature in the range of 700° to 850° F., a pressure in the range of 0 to 1000 p. s. i. g., and a space velocity in the range of 0.2 to 2.0 v./v./hr., whereby a conversion to 1050° F. and lighter material of said first mixture in the range of 30 to 50 vol. percent is obtained and a hydrogen donor diluent is secured, separating from the material so treated a fraction boiling above 400° F. displaying hydrogen donor properties, mixing said fraction with ½ to 1 vols. of additional amounts of said heavy oil to form a second mixture, thermally treating said second mixture under hydrogen donor diluent cracking conditions, said conditions including a temperature in the range of 700° to 900° F., a pressure in the range of 0 to 1000 p. s. i. g., and a throughput in the range of 0.5 to 5.0 v./v./hr., whereby a conversion to 1050° F. and lighter material of said second mixture in the range of 50 to 80 vol. percent is obtained, and separating the thermally treated mixture to obtain various product fractions.

3. A residual oil conversion process which comprises mixing 25 to 50% of a residuum feed with ½ to 3 volumes of an aromatic-naphthenic containing diluent oil suitable for being converted to a hydrogen donor diluent and boiling within the limits of 400 to 100° F., hydrocracking the resulting mixture in the presence of a hydrogenation catalyst and 300 to 1000 s. c. f. of hydrogen per barrel of mixture at a 1050° F.— conversion in the range of 30 to 60% and at a pressure below 1000 p. s. i. g., separating from the hydrocracked mixture material boiling below about 400° F., mixing the remainder of said hydrocracked mixture having an appreciable quantity of material suitable as a hydrogen donor diluent with the remainder of said residuum feed, thermally treating the second mixture so formed under hydrogen donor diluent cracking conditions at a 1050° F.— conversion in the range of 40 to 90%, separating the thermally cracked mixture to obtain a fraction boiling in the range of about 430° to 700° F., and returning said last named fraction to the hydrocracking zone as said aromatic-naphthenic fraction.

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