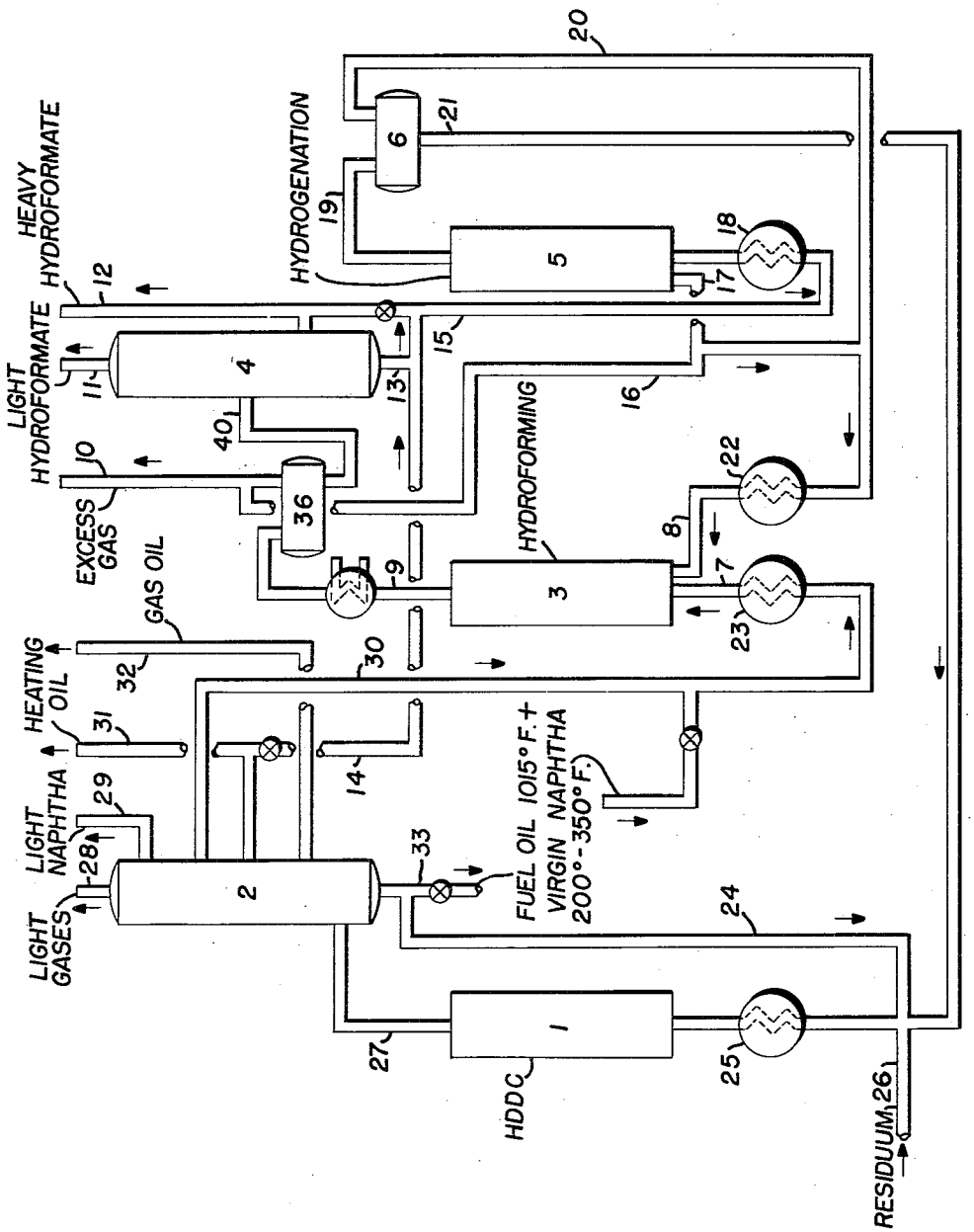
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HYDROCARBON OIL CONVERSION PROCESS

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HYDROCARBON OIL CONVERSION PROCESS

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This invention relates to the art of converting hydrocarbon oils. It is concerned with a method for upgrading heavy petroleum oils in the nature of vacuum residua and for producing a high quality product suitable for use as a motor fuel. In its more specific aspects, the present invention reforms naphthas to obtain gasolines of high octane ratings while concurrently upgrading residual oils by hydrogenolysis. The present invention proposes to utilize the hydrogen and the highly aromatic polymer produced by hydroforming operations to transform low value residua into middle distillates.

It is known by the art to upgrade hydrogen-deficient oils such as vacuum residua, tars, asphalts, etc. to more valuable liquid distillates by thermally treating the hydrogen-deficient material in admixture with a hydrogen donor diluent material. The donor diluent is a material, aromatic-naphthenic in nature, that has the ability to take up hydrogen in a hydrogenation zone and readily release it to a hydrogen-deficient oil in a thermal cracking zone. The hydrogen donor diluent is specially prepared by partially hydrogenating, by conventional means, a selected petroleum oil fraction that is predominantly composed of aromatic-naphthenic constituents having hydrogen transferring characteristics. In this manner of hydrocracking of oils, the oil being upgraded is not contacted directly with hydrogenation catalyst and does not, therefore, impair its activity by contamination. The amount of concomitant light gases and coke produced by this hydrogen donor diluent cracking (HDDC) process is relatively small, usually being in the order of about 5 to 10%.

The prior art has suggested, for example, that a thermal tar boiling in the range of about 700° to 900° F. obtained by the thermal cracking of catalytic cycle oils will serve admirably as a hydrogen donor diluent. Such a material contains condensed ring aromatics in sufficient quantities to economically serve as a hydrogen carrier. The material is partially hydrogenated such that there is added to it some easily removable hydrogen atoms but not enough to convert the aromatics in the material substantially to naphthenes. This material, after being partially hydrogenated, is admixed with an oil such as a vacuum residuum and the mixture is thermally treated, whereby the hydrogen is transferred from the partially hydrogenated material to the residuum, thereby upgrading the residuum. It is believed that the donor diluent operates by yielding hydrogen atoms to the radicals that have been created from the residuum by the thermal treatment, thereby preventing condensation and/or polymerization of the radicals.

In normal HDDC operations, as the donor diluent material is substantially unaltered as it passes through the process, it is customary to recycle the material so that it is used over and over again as a hydrogen carrier. Losses of about 2 to 20% of the diluent material have been encountered due, perhaps, to some cracking of the diluent and to imperfect separation techniques.

It has now been discovered that the polymer produced by catalytic naphtha-reforming operations contains a type of compound suitable for use as a hydrogen donor or carrier and in quantities sufficient to be economically attractive. Also, it has been found that the light gases produced during the hydroforming operations contain a sufficiently

high percentage of hydrogen to serve to partially hydrogenate the polymer material in a hydrogenation zone.

It is an object of the present invention to use materials from catalytic naphtha-reforming operations, normally surplusage in a refinery, as a means to upgrade high boiling, low value oils to more economically desired distillates, e. g., gas oils suitable for catalytic cracking and naphthas suitable for hydroforming. Because of the diluent loss previously mentioned, the integration of the two types of hydrocarbon oil conversion processes, e. g., residuum upgrading and naphtha reforming, is accomplished by maintaining select optimum boiling range division of the products, recycle rates, treating temperatures, etc.

As is known by the art, hydroforming processes normally have a high yield of reformed product based upon feed with only a small percentage, say 1 or 2%, of the naphtha feed being degraded to heavier material, e. g., polymer, by condensation and polymerization reactions. By maintaining optimum conditions, however, the present invention is able to maintain a sufficient quantity of donor diluent in the residuum upgrading or HDDC step of the process of this invention by use of the polymer with, perhaps, some of the heating oil produced during the HDDC step.

To produce a heavy polymer in the hydroforming step, to serve as a donor, a wider cut of naphtha from HDDC step is cycled and fed to the hydroformer than is usual in hydroforming. For example, 350° F. is the usual endpoint for virgin feeds but in the present invention a 450° to 550° F. endpoint thermal naphtha is fed to the hydroformer. The 375° plus material is the source of heavy recycle polymer as diluent for HDDC. The octane number of the thermal naphtha is improved by the hydroforming from about 60 to 90. Research O. N., sulphur is removed and the gasoline is stabilized.

Thus a primary object of the present invention is to convert and upgrade hydrocarbon oils, particularly petroleum derived oils. Another object is to upgrade selected oil fractions, particularly heavy naphthas and residual oil fractions, to liquid distillates of improved quality. Still another, more particular, object is to devise a process whereby low octane naphthas are reformed to yield high octane products and whereby hydrogen deficient oils are upgraded to light and middle distillates. The hydrogen deficient oils that may be treated by the process of this invention include coal tars, shale oils, extracts, tars, asphalts, cycle stocks, whole crudes, distillate and residual fractions therefrom, or mixtures thereof.

These and other objects and advantages will more clearly appear as the attached drawing, forming a part of this specification, is described in detail. The drawing schematically portrays one preferred embodiment of the invention, designed to attain its objects.

Generally the objects of this invention are met by passing a virgin heavy naphtha and a heavy thermal naphtha through a catalytic reforming zone, preferably a fluid bed hydroforming zone with regeneration facilities containing a molybdenum oxide catalyst. The effluent from the reforming zone is separated to obtain a hydrogen-rich gas, high octane naphthas and a somewhat higher boiling hydrocarbon stream rich in aromatic-naphthenic constituents, e. g., polymer. The hydrogen rich gas is used to partially hydrogenate the polymer in a conventional hydrogenation zone. This hydrogenation zone in a preferred embodiment of this invention uses as the hydrogenation catalyst the same catalyst used for the reforming operation, e. g., molybdenum oxide, and the hydrogenation is affected by operating at somewhat lower temperatures. The resulting partially hydrogenated liquid product, e. g., hydrogen donor diluent, is admixed with a hydrogen-deficient oil and subjected to thermal treating whereby the donor diluent gives up

hydrogen to the hydrogen-deficient oil while the hydrogen-deficient oil is being thermally cracked. The thermally treated mixture is then separated to obtain: a residual fraction, a portion of which can be recycled for further thermal treating; a gas oil fraction boiling in the range of about 600° to 1015° F., suitable as feed for catalytic cracking; a heating oil fraction, a portion of which may be hydrogenated to save as hydrogen donor diluent; a heavy naphtha fraction boiling in the range of about 200° to 550° F. which is transferred to the hydroformer to be treated therein; and a light naphtha fraction boiling in the range of about C_4 to 200° F. which is of suitable quanity for direct marketing with very little further treatment.

The feed streams to the process of this invention may be derived from any convenient source. Advantageously both streams can be obtained from the initial separation of a whole crude. Thus the hydrogen-deficient material can be the vacuum bottoms from the primary fractionation of the crude and the material for reforming can be the virgin heavy naphtha boiling in the range of about 200° to 550° F. Virgin naphtha is preferred as it will generate sufficient quantities of hydrogen to meet the demands of the process.

There are known in the art several catalytic reforming processes such as fixed and fluid bed processes, regenerative and nonregenerative processes, high and low pressure processes, and processes using different types of catalyst such as platinum, molybenum, etc. Practically all of the reforming processes are carried out in the presence of a recycled heat-carrying gas stream which aids in controlling the severity of the reformation and promotes catalyst life. Broadly, any hydroforming process is suitable for use with the process of this invention. Preferably, however, a fluid bed hydroformer with a cataiyst regeneration system is used. Also preferably, a molybdenum oxide catalyst supported on alumina in particulate form is used as a catalyst as this type of catalyst is particularly resistant to contamination and deactivation. Further, this catalyst will serve as a hydrogenation catalyst and if used as such allows the hydrogenation catalyst to be regenerated in a regenerator common to the fluid bed hydroformer.

Referring now to the drawing, the major items of equipment shown are hydrogen donor diluent cracking reactor **1** with a fractionation column **2**, for the separation of the materials treated in the HDDC step, a hydroformer **3** with a fractionator column **4**, and a hydrogenation vessel **5** with a separator **6**.

The process will be described using a fluid bed hydroformer as an example, although the catalyst regenerator is not shown. This method of hydroforming is well known by the art. The operating conditions applicable to the process of this invention are conveniently summarized in Table I, presented hereinafter.

The naphthas to be reformed are introduced into the hydroformer, after being preheated, by line **7**. The heat-carrying recycle gas is supplied to the hydroformer by line **8**. The conditions are selected so as to obtain the desired degree of octane improvement of the naphthas. Effluent from the hydroformer is transferred to a separation system via line **9**. Light gases are removed from the hydroformer effluent by separator **36**. The condensed material is then transferred by line **40** to fractionator **4** wherein light hydroformate is separated and removed by line **11**. Line **12** removes heavy hydroformate boiling in the range of about 250° to 400° F. Line **13** removes the condensation and polymerization material, e. g., polymer formed by the hydroforming reaction. This polymer is transferred by lines **14** and **15** to the hydrogenation vessel. A portion of the heavy hydroformate may also be transferred to the hydrogenation vessel as it will contain some material suitable as a hydrogen donor. The gases in line **10** which may contain about 60 to 85% hydrogen are transferred to the hydrogenation vessel by lines **16** and **17**. The feed to the hydrogenation vessel may be suitably preheated in heat exchanger **18** as by heat exchange with various streams of the process or with flue gases, etc.

The hydrogenation vessel may be of a conventional type that will secure sufficient partial hydrogenation of the polymer material. For example, a fixed bed hydrogenation vessel using a nickel tungsten sulfide catalyst as 3/16" pills will give the proper degree of hydrogenation of the diluent when operated at conditions in the range of 650° to 800° F., 200 to 1000 p. s. i. g. and 0.2 to 2.0 v./hr./v.

Preferably, however, a fluid bed hydrogenator is used operating with the same catalyst as the hydroformer, e. g., molybdenum oxide. With this preferred arrangement, if the hydrogenation catalyst becomes fouled, it can then be regenerated in the hydroformer regenerator.

The hydrogenated donor diluent is transferred by line **19** to a separator wherein light gases are removed by line **20** and passed to the hydroformer. The hydrogenated material is then transferred to the HDDC reactor by line **21**.

The materials supplied to the hydroformer are, of course, suitably preheated to supply the necessary heat for the reaction. The light gases are preheated in heat exchanger system **22** which includes heat exchange with various streams of the process and final heating furnaces that heat the gas to about 1200° F. The naphtha streams are similarly preheated in heat exchange means **23**. Also, in a fluid bed hydroforming process, heat will be obtained through the catalyst from the regeneration system.

The material introduced into the HDDC reactor, including bottoms recycled by line **24**, the hydrogen-deficient residua supplied by line **26** and the donor diluent supplied by line **21**, are also heated in a heat exchange means **25** to maintain the necessary cracking temperature. Each of these streams can, of course, be separately preheated in such a manner that they will convey the highest quantity of heat possible to the cracking reactor short of being unduly thermally degraded by high temperatures. From the heat exchange means **25**, the materials are introduced into a soaking drum **1**, wherein they are maintained under conditions of time, temperature and pressure sufficient to attain the desired degree of conversion and hydrogen transfer. Normally a coil and drum arrangement will be used for the HDDC reaction. However, in many applications, a heating coil or furnace alone will be sufficient to carry out the reaction.

The cracked materials are then transferred by line **27** to fractionator **2**. Light gases are separated and removed from the fractionator by line **28** and a light naphtha fraction boiling in the range of about C_3 to 200° F. is removed by line **29** as product. Line **30** conveys to the hydroformer a heavy thermal naphtha fraction boiling in the range of about 200° to 550° F. that contains a major portion of the spent donor diluent. A heating oil fraction is removed as product by line **31**. To aid in the maintenance of the diluent balance in the process, a portion of this heating oil fraction is recycled by line **14** to the hydrogenation zone, although in certain applications it may not be necessary to do this. A gas oil boiling up to about 900° to 1100° F. is removed by line **32** and may advantageously be catalytically cracked to secure further quantities of high octane gasoline. A major portion of the remaining heavy bottoms are transferred by line **24** to the HDDC unit for further treatment. A portion of these bottoms amounting to about 5 to 25% based on residua feed are bled from the process by line **33** in order to prevent excessive build-up of contaminants, ash constituents, etc.

The endpoint of the heavy thermal naphtha in line **30** can be varied from about 450° to 550° F. as desired to provide and maintain the balance in the process of aromatic-naphthenic materials hydrogenated to form the hy-

drogen donor diluent. The cut point will depend primarily on the type of feed and extent of conversion in the HDDC step. The heating oil recycle ratio will, of course, change in accordance with the change in heavy naphtha cut point.

The following Table I summarizes the pertinent range of operating conditions applicable to the process of this invention and presents a specific example of operating conditions. Table II illustrates the products that may be obtained from this process when using the type of feed stocks indicated and operating in accordance with the example in Table I.

TABLE I

Operating Conditions	Range	Example
HDDC unit (coil and drum):		
Temperature, °F	800 to 950	850
Pressure, p. s. i. a.	200 to 1,000	400
Throughput, v./hr./v.	0.5 to 10	2.0
Donor diluent/residuum ratio	0.1 to 3	5
1,000° F. minus Conversion,[1] Vol. Percent	40 to 70	60
Hydroforming unit (Fluid hydroformer with continuous regeneration):		
Catalyst		[2]
Temperature, °F	850 to 975	900
Pressure, p. s. i. a.	100 to 500	215
Catalyst/oil	0.2 to 2.0	0.8
Throughput, v./hr./v.	0.3 to 1.5	0.8
Research Octane of C_5+	80 to 98	90
Hydrogenation unit (Fluid Bed):		
Catalyst		[2]
Temperature, °F	650 to 800	720
Pressure, p. s. i. a.	175 to 500	215
Throughput, v/hr./v	0.2 to 2.0	0.5
H_2 consumed, S. C. F./bbl. diluent	300 to 2,000	800
Diluent boiling range, °F	400 to 750	400–550

[1] Of total feed to unit including donor diluent; 1000° F. plus conversion equals 100 vol. percent feed minus vol. percent of products boiling above 1000° F.

[2] 5–10 Wt. percent MoO_3 on alumina.

TABLE II

	Vacuum Residua	Virgin Naphtha
Source	12.9° West Texas Vacuum.	West Texas Crude.
Boiling range ° F	1,000° F.+	200–350.
Gravity, ° API	7.5	52.7.
Conradson Carbon, Wt. percent	21.4	
H/C atomic ratio	1.51	
Aromatics, Vol. percent		12.
Paraffins, Vol. percent		41.
Paraffins, percent		47.
Sulfur, wt. percent		0.15.

Net Products, percent based on total fresh feed, equal volumes of residua and naphtha:		
C_3 and lighter gases (51% H_2)	wt. percent	7
C_4–200° F. light naphtha (70 octane)	vol. percent	5
C_5–350° F. light hydroformate (90 octane)	do	60
350°–430° F. heavy hydroformate (100 octane)	do	2
450°–650° F. heating oil (40 Diesel Index)	do	15
650°–1015° F. gas oil	do	10
1015° F.+fuel oil	do	15
Coke	wt. percent	2
10# R. V. P. gasoline, with extraneous C_1 addition	vol. percent	73
Internal Flows:		
1015° F.+bottoms to HDDC/bbl. residua	bbl.	0.90
Donor Diluent to HDDC/bbl. residua	bbl.	0.5
200°–450° F. thermal naphtha to hydroforming/bbl. virgin naphtha	bbl.	0.7
Recycle gas [1] (75+ H_2) to hydroforming/bbl. virgin naphtha	S. C. F.	4000
Polymer to hydrogenation/bbl. residuum	bbl.	0.3
Heating oil to hydrogenation/bbl. residuum	bbl.	0.2
Gas (75% H_2) to hydrogenation/bbl. polymer and heating oil	S. C. F.	20,000

[1] Includes gas from hydroformer product and from hydrogenator.

From the preceding description, it can be seen that the present invention advantageously utilizes the normally waste materials produced by a hydroforming process to upgrade hydrogen deficient, low value oils.

Having described the 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 oil conversion process which comprises reforming in a catalytic reforming zone a heavy virgin naphtha boiling in a range within the ilmits of 200° to 550° F. in the presence of a reforming catalyst and free-hydrogen containing gas to obtain a hydrogen rich gas, naphthas of substantially higher octane and a higher boiling hydrocarbon stream rich in aromatic-naphthenes, reheating and returning a portion of said hydrogen rich gas to said catalytic reforming zone as said free hydrogen containing gas, partially hydrogenating at least a portion of said higher boiling hydrocarbon stream using said hydrogen rich gas as a source of hydrogen to obtain a partially hydrogenated hydrogen donor diluent, admixing 1 volume of residual oil with 1 to 3 volumes of said hydrogen donor diluent, subjecting the resulting admixture to conditions of hydrogen donor diluent cracking to obtain lighter products including a heavy thermal naphtha boiling in a range within the limits of about 200° to 550° F., and light gas oils and passing said thermal naphtha to said catalytic reforming zone to be reformed therein along with said virgin naphthas, the end boiling points of said virgin and thermal naphthas being adjusted to maintain the proper balance of said hydrogen donor diluent in the process.

2. The process of claim 1 wherein a portion of said light gas oils are partially hydrogenated along with said higher boiling hydrocarbon streams to obtain said hydrogen donor diluent.

3. A process for reforming naphthas and for upgrading hydrogen deficient petroleum oils comprising hydroforming a virgin naphtha boiling in the range of about 200 to 550° F., and a thermal naphtha obtained as hereinafter described in a hydroforming zone containing a fluid bed of hydroforming catalyst and operating at a temperature in the range of 850° to 975° F., at a pressure in the range of 100 to 500 p. s. i. a., and at a throughput in the range of 0.3 to 1.5 v./hr./v. to obtain a hydrogen containing gas, a light hydroformate, a heavy hydroformate boiling in the range of about 350° to 430° F., and polymer, circulating said hydroforming catalyst to a fluid bed oxidation-regeneration zone and back to maintain the catalytic activity of said hydroforming catalyst, hydrogenating said polymer in a hydrogenation zone containing a hydrogenation catalyst, using at least a major portion of said hydrogen containing gas as a source of hydrogen and operating at a temperature in the range of 650° to 800° F., a pressure in the range of 175 to 500 p. s. i. a., and at a throughput in the range of 0.2 to 2.0 v./hr./v. to obtain a partially hydrogenated donor diluent, admixing said partially hydrogenated donor diluent with a heavy petroleum oil in a proportion in the range of about 0.1 to 3 volumes diluent/volume of oil, thermally treating the resulting mixture in a thermal treating zone operating at a temperature in the range of about 800° to 950° F., at a pressure in the range of about 200 to 1000 p. s. i. a., and at a throughput in the range of about 0.5 to 10 v./hr./v. to obtain light naphthas, a heavy thermal naphtha boiling in the range of about 200° to 550° F., higher boiling distillate fractions and residue boiling above a temperature in the range of 900° to 1100° F., and passing said heavy thermal naphtha to said hydroforming zone to be treated therein.

4. The process of claim 3 wherein said hydrogenation zone contains a fluid bed of molybdenum catalyst.

5. The process of claim 3 wherein said heavy petroleum oil includes heavy residual oils boiling above about 900° F.

6. The process of claim 3 wherein at least a portion of said higher boiling distillate fractions is transferred to said hydrogenation zone.

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