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PROCESS FOR THE UPGRADING OF HYDROCARBONS
BY HYDROGEN-DONOR DILUENT CRACKING
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PROCESS FOR THE UPGRADING OF HYDROCARBONS BY HYDROGEN-DONOR DILUENT CRACKING

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4 Claims. (Cl. 196—50)

The present invention relates to the conversion of residual oil fractions and particularly to a process and a system for converting residual oils such as reduced crude petroleum to more volatile products by the thermal cracking of the oils in the presence of a hydrogen donor diluent.

Hydrogen donor diluent cracking (HDDC) has been previously proposed. The purpose in donor diluent cracking is to cause hydrogen retained by the diluent to transfer to the heavier residual fractions being cracked and in this way to prevent the formation of coke which is the usual product of ordinary thermal cracking or coking operations. The HDDC process is more fully illustrated by co-pending application, "Upgrading of Hydrocarbon Oils," S. N. 365,335, filed July 1, 1953, now abandoned, by Arthur W. Langer, Jr. The hydrogen donor method offers a possibility of increasing the liquid yield over that attainable from the ordinary coking processes. A difficulty with the hydrogen donor process is that in normal refinery operations the quantity of naphthenic streams suitable for hydrogen transfer is limited. In fact, it is not easy to find enough suitable aromatic streams which can be hydrogenated to serve as hydrogen donors. For this reason, the previously proposed processes have utilized the standard recycling of streams method to obtain enough material suitable for hydrogenation.

The previous schemes, however, embody recycling of various boiling range cuts which are not entirely suitable for the purpose of hydrogenation and the consequent hydrogen transfer operation. That is, the proposed streams do not contain a high enough proportion of suitable aromatics to act as hydrogen carriers. Hence, when the thermal operation takes place some of the residuum is left unaltered. Another difficulty with past schemes is that one of the products of the operation is usually intended for use as feed for catalytic cracking. Very often the material which is used for rehydrogenation, to form a hydrogen donor, is identical with that which is put out as product for catalytic cracking. These requirements are somewhat contradictory since the raw material for hydrogen donor production is desired to be predominantly aromatic, while the catalytic cracking feed stock is preferably predominantly non-aromatic.

This invention is based upon the discovery that both these difficulties can be obviated by incorporating into the process a suitable step of aromatic separation. The separated aromatics or predominantly aromatic constituents are used for rehydrogenation while the aromatic-poor product is sent to the catalytic cracking operation or to other operations using gas oils and similar products. It will be appreciated that by this extraction step, i. e., concentration of desirable aromatics in the hydrogen donor diluent, there will be a marked improvement in the quality of the products from the HDDC system. This improvement results from two factors. First, because of the improved quality of the hydrogen donor diluent charged to the HDDC system, there will be less thermal degradation of the heavy residual fractions being cracked.

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Second, and of equal importance, the catalytic cracking feed stock produced will be greatly improved by elimination of the aromatics. Formerly, removal of aromatics from catalytic feed stocks was not attractive because no use existed for the extracted aromatics. This invention, however, makes novel and desirable use of aromatics removed from catalytic cracking feed stocks. The process of this invention is illustrated diagrammatically in the attached drawing which forms a part of this specification.

10 A primary object of the present invention is to make it possible to convert all, or substantially all, of even the heaviest hydrocarbon oils and the most refractory to lower boiling or lighter, and hence more valuable, hydrocarbon products. Another object is to improve greatly the quality of the products produced by hydrogen donor diluent cracking of heavy hydrocarbon oils. A further object is to reduce substantially the production of coke when heavy residua are thermally cracked and to approach 100 percent conversion of the residua to useful gas oils. The invention aims particularly for the increased production of gas oil. This gas oil may be used as heating fuel, diesel fuel or fuel oil but is intended to be used primarily as catalytic cracking feed stock. A more specific object of this invention is to increase the efficiency and practicability of the hydrogen donor process by incorporating into that process a step of aromatic separation. Further objects and advantages will appear more clearly as this description proceeds.

Generally stated, the objects of this invention are obtained by mixing a heavy residuum feed with a recycled partially hydrogenated thermal tar rich in selected aromatics. The mixture is then heated and passed through a thermal cracking and soaking zone. After allowing a suitable time for conversion, the mixture is separated by fractionation essentially into lighter hydrocarbons, gas oils, a diluent fraction and a heavy bottoms fraction. The diluent fraction is used as a source of aromatics for the hydrogen donor diluent. It is possible, however, to use all or part of the bottoms fraction as a source of these aromatics. If so, then it would not be necessary to make a diluent cut. The diluent fraction or a portion thereof is transferred to an aromatic extraction or separation zone where a suitable selection of aromatics is made. The selected aromatics are then partially hydrogenated by conventional means to yield the donor diluent. The process is capable of many variations which will appear below as the embodiment illustrated in the drawing is described in detail.

The prior art has suggested that various hydrogenated aromatic chemicals may have utility as hydrogen carriers for processes like the HDDC. The prior art has mistakenly supposed, however, that the more highly hydrogenated materials are superior. Recently this has been found to be an erroneous and unwarranted assumption. A heavy oil fraction, boiling above 500° F. up to about 1100° F., containing substantial and preferably at least major portions of condensed ring aromatics and having added thereto some easily removable hydrogen atoms, but not enough to approach saturation, shows outstanding utility as hydrogen donor material. The more highly hydrogenated aromatics show much less activity. Moreover, pure or substantially pure chemical compounds or hydrogenated products derived from pure compounds are usually relatively very expensive and their use as hydrogen donor diluents is not economically justifiable.

It has been discovered that there are some highly aromatic condensed ring fractions available in most crude oils, and especially in heavy residua, so that the feed stocks themselves usually can supply a major proportion of the required diluent. Refinery streams which are rich in high boiling easily condensed aromatics may be partially hydrogenated by adding thereto from about 200

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to 2000 s. c. f. of hydrogen per barrel of diluent. These streams will make excellent diluents. Thermal tars boiling in the range of 700 to 900° F. are particularly preferred. Thus, cycle stock fractions or catalytic feed stocks may be used as a source of donor material without special thermal cracking. This type of material is particularly desired because they are usually surplusage in refinery operations and are, therefore, a cheap source for the donor diluent.

In general, the condensed ring aromatics that are selected for partial hydrogenation are those which are quite stable to cracking under the reaction conditions. They are susceptible to relatively easy hydrogenation and dehydrogenation. Complete hydrogenation produces a much less effective donor. Ordinarily it is preferred to recycle a 700 to 900° F. cut of a thermal tar, i. e. a thermally cracked cycle oil from catalytic cracking bottoms, after its partial hydrogenation. By this method a diluent material can be used over and over as long as its aromatic structure is not changed. Usually however the recycled cuts do not contain a sufficiently high percentage of condensed ring compounds to accomplish effectively the task of hydrogen donation. This invention proposes that thermal tars of the type mentioned above used as hydrogen donor material can be made much more effective by suitable aromatic extraction, and thus concentration of the aromatic donor material. The process of this invention is capable of using any one of several well-known aromatic extraction or concentration processes.

To make the invention more clear the attached drawing will now be discussed in detail.

The residuum feed enters the process through line 10 and is mixed with the recycled hydrogenated thermal tar supplied by line 11. Recycled heavy bottoms from the fractionation stage can also be mixed with the feed at this point, either through a separate line or through the thermal tar line. A preferred embodiment of the invention is to recycle the unconverted bottoms from the fractionation stage. The recycled bottoms will amount preferably to about 0.5 to 2.0 volumes of bottoms per volume of feed and the hydrogenated tar will amount to 0.5 to 1.0 volumes per volume of feed. Of course, depending upon the type of feed, operating conditions, degree of hydrogenation and like factors, the recycled hydrogenated tar could vary anywhere from 0.1 to 2.0 volumes of tar per volume of feed. The mixture is then passed to a thermal cracking zone. Any suitable type of equipment could be used but for the purpose of this illustration a coil and drum arrangement is depicted. The mixture is heated in the furnace 1 and passed by line 12 to the soaker 2 where it remains for a suitable time. The conditions for cracking in extreme cases may vary from temperatures of 500 to 1200° F., pressures of 100 to 3000 p. s. i. g. and residence times of 0.1 to 5.0 v./v./hr., but for a topped virgin crude feed, 800 to 850° F., 300 to 400 p. s. i. g. and 1 to 3 v./v./hr. are preferred. It is understood, of course, that residence time in part, is a function of the cracking temperature.

After this treatment, the cracked mixture is transferred, via line 13, to a fractionator 3 (or a flashing chamber or is partially condensed) in order that the lighter gas oils and gasolines can be separated from the heavy unconverted residuum and the donor material. As shown in the drawing, the cracked material is divided into four components. Gas is removed by line 14, a gas oil fraction by line 15 as product, a diluent cut by line 16 and the bottoms by line 17. The diluent cut can have a wide variation in boiling range, say from 400° to 1100° F., depending upon the processed material and operating conditions, but a 700° to 900° F., range is preferred. A diluent cut need not be made at all. Instead, all or part of the bottoms can be sent to an aromatic extraction unit to be described.

Several variations in the flow can be made at this

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point. As just mentioned the bottoms can be transferred by lines 17, 27, 18 and 16a, to the aromatic extraction unit, all or part can be recycled by line 25 to the feed, or part can by-pass the extraction unit by lines 27 and 26 to the hydrogenator 6. The same is true of the diluent cut, if one be made. All or part of it carried by lines 16 and 16a, can be used as the source of aromatics, can be hydrogenated by passing it to the hydrogenator 6 via lines 16, 18 and 26, or can be recycled by line 16, 18, 27 and 25 to the feed.

Because the aim of this invention is to maintain an aromatic level in the hydrogenated tar, only a portion of the diluent cut or bottoms need be used as a feed to the aromatic extraction plant. For a topped virgin crude feed, the amount of a 700-900° F. diluent cut sent to extraction will amount to 0.6 to 1.5 volume of cut per volume of feed. For the same feed, the recycled bottoms to the feed will amount to about 1 volume of bottoms per volume of feed and about 0.5 to 1 volume of 700-900° F. cut will be passed directly to the hydrogenator.

As mentioned, it is possible to use a variety of aromatic separation plants or processes using extraction media such as sulfur dioxide, antimony trichloride and furfural. For the purpose of illustration a simplified phenol extraction system is used. The diluent cut feed enters the extracting column 4 by line 16a and is mixed with recycled phenol supplied by line 20. The raffinate is removed by line 19 to stripping tower 7 where the phenol is separated and returned by line 30 and the aromatic-poor oil is removed by line 29 as product of the process. The extract leaves column 4 by line 21 and goes to a stripper 5 where the phenol is separated and returned by line 20 and the aromatic-rich oil is removed and passed by line 22 to the hydrogenator, the hydrogenator being supplied with hydrogen from an external source by line 23.

The thermal tar diluent is hydrogenated by adding to the diluent about 200 to 6000 cubic feet of hydrogen per barrel of the diluent and passing the mixture over a suitable hydrogenation catalyst. Since there are likely to be appreciable quantities of sulfur present in the diluent, 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 with conventional temperatures may be used. The conditions, in any case, should be so chosen that the diluent is only partially hydrogenated. The diluent 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 a naphthene. With 700 to 900° F. thermal tar of average molecular weight around 300 or so, hydrogen consumption may run from about 250 to 1000 s. c. f. per barrel. The consumption of hydrogen may vary considerably, however, from as little as 100 to as much as 2000 or more s. c. f./bbl. The important criterion is that the hydrogenation be carried approximately to that stage at which hydrogen transfer, in the thermal operation, to the cracked products reaches a maximum. After being hydrogenated, the diluent is passed by lines 24 and 11 to the feed.

Since the materials are recycled, it may be necessary to provide for a purge and make-up to prevent the excessive build-up of contaminants, like metals and ash, in the recycled streams. For this reason a purge line 28 is indicated in the recycled bottoms line 17 and a make-up line 31a is shown for the recycled diluent line. Line 31b may be used to add make-up diluent to the extraction column 4. By adding make-up diluent through line 31b the load on the hydrogenator 6 can be reduced since it handles a diluent higher in the desired aromatics and consequently would handle a lesser amount of diluent. This fresh make-up diluent can consist of any refinery stream that contains suitable proportions of aromatics. Thermal tar boiling in the range of 700-900° F. from a catalytic

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cracking unit is particularly suitable but other suitable materials are lube oil extracts, clarified oil, tars and asphalts from the deasphalting of residua, and the like.

For the described process, the following material balance could be expected for a feed stock having the following specifications: 8° API gravity, 21 wt. percent Conradson carbon, 1000° F. initial boiling point:

Feed-----	bbls.--	1000
Recycle bottoms, 1000° F. +boiling range	bbls.--	1000
Diluent cut made, 700 to 900° F. boiling range-----	bbls.--	1000
Diluent recycle to feed, 700 to 900° F. boiling range-----	bbls.--	800
Hydrogen consumption-----	s. c. f.--	400,000
Make-up thermal tar-----	bbls.--	200
Yields:		
Dry gas-----	s. c. f.--	330,000
Gasoline, C ₄ -430° F. boiling range--	bbls.--	390
Gas oil, 430 to 1000° F. boiling range	bbls.--	620

Having described a preferred embodiment of the invention, it is to be understood that the invention is not to be limited by the description but only by the following claims.

What is claimed is:

1. In a process for upgrading heavy hydrocarbonaceous oils which comprises the steps of partially hydrogenating in a hydrogenation zone a recycled hydrocarbon stream obtained as hereinafter described to form a hydrogen donor diluent, admixing said donor diluent with a heavy oil feed and a recycled bottoms fraction, thermally cracking the resulting mixture, and separating the cracked mixture into at least a light fraction as product, a diluent fraction boiling between about 700° and 900° F. and a bottoms fraction; the improvement which comprises passing at least a portion of said diluent fraction to an aromatic separation zone, separating from said portion of diluent fraction a concentrate containing substantially increased proportions of condensed ring aromatics by selective solvent treatment and passing said concentrate to said hydrogenation zone to supply at least a portion of said recycled hydrocarbon stream.

2. The process of upgrading heavy hydrocarbons which comprises mixing a heavy hydrocarbon feed with a partially hydrogenated hydrogen donor diluent including a

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high boiling cycle stock from catalytic cracking of gas oil, subjecting the mixture to conditions conducive to thermal cracking in the absence of catalyst and free hydrogen, separating from the thermally treated mixture a relatively heavy distillate fraction, separating from at least a portion of said heavy distillate fraction in an aromatic extraction zone a hydrocarbon stream containing substantial proportions of aromatics, partially but not completely hydrogenating said hydrocarbon stream in a hydrogenation zone in the presence of a sulfur resistant catalyst and recycling and blending the hydrocarbon stream so hydrogenated to supply at least a portion of said hydrogen donor diluent.

3. The process of claim 2 which comprises admixing said hydrogen donor diluent with said feed in proportions of 0.1 to 2 vols. of diluent/vol. of feed, when said heavy distillate fraction boils in a range above 700° F. and when about 100 to 2000 s. c. f. of hydrogen/bbl. of said hydrocarbon stream is added in said hydrogenation zone.

4. In a hydrogen donor diluent conversion process wherein a heavy oil is thermally cracked in the absence of the catalyst and free hydrogen, in admixture with a hydrogen donor diluent, wherein spent hydrogen donor diluent is recovered and regenerated by partial hydrogenation and recycled, the improvement which comprises subjecting at least a part of said spent hydrogen donor diluent to an aromatic separation step to concentrate the desirable aromatic polycyclic ring structures therein and thereafter hydrogenating said concentrate by adding thereto 250 to 1000 s. c. f. per barrel of hydrogen in the presence of an active hydrogenation catalyst whereby the effective aromaticity and the hydrogen donor properties of the diluent are substantially improved.

References Cited in the file of this patent

UNITED STATES PATENTS

2,363,782	Frey -----	Nov. 28, 1944
2,367,474	Stewart -----	Jan. 16, 1945
2,426,929	Greensfelder -----	Sept. 2, 1947
2,620,293	Blue et al. -----	Dec. 2, 1952
2,701,783	Long -----	Feb. 8, 1955

OTHER REFERENCES

45	Sachanen: "Chemical Constituents of Petroleum," page 229 (1945), Reinhold Publishing Co., New York.
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