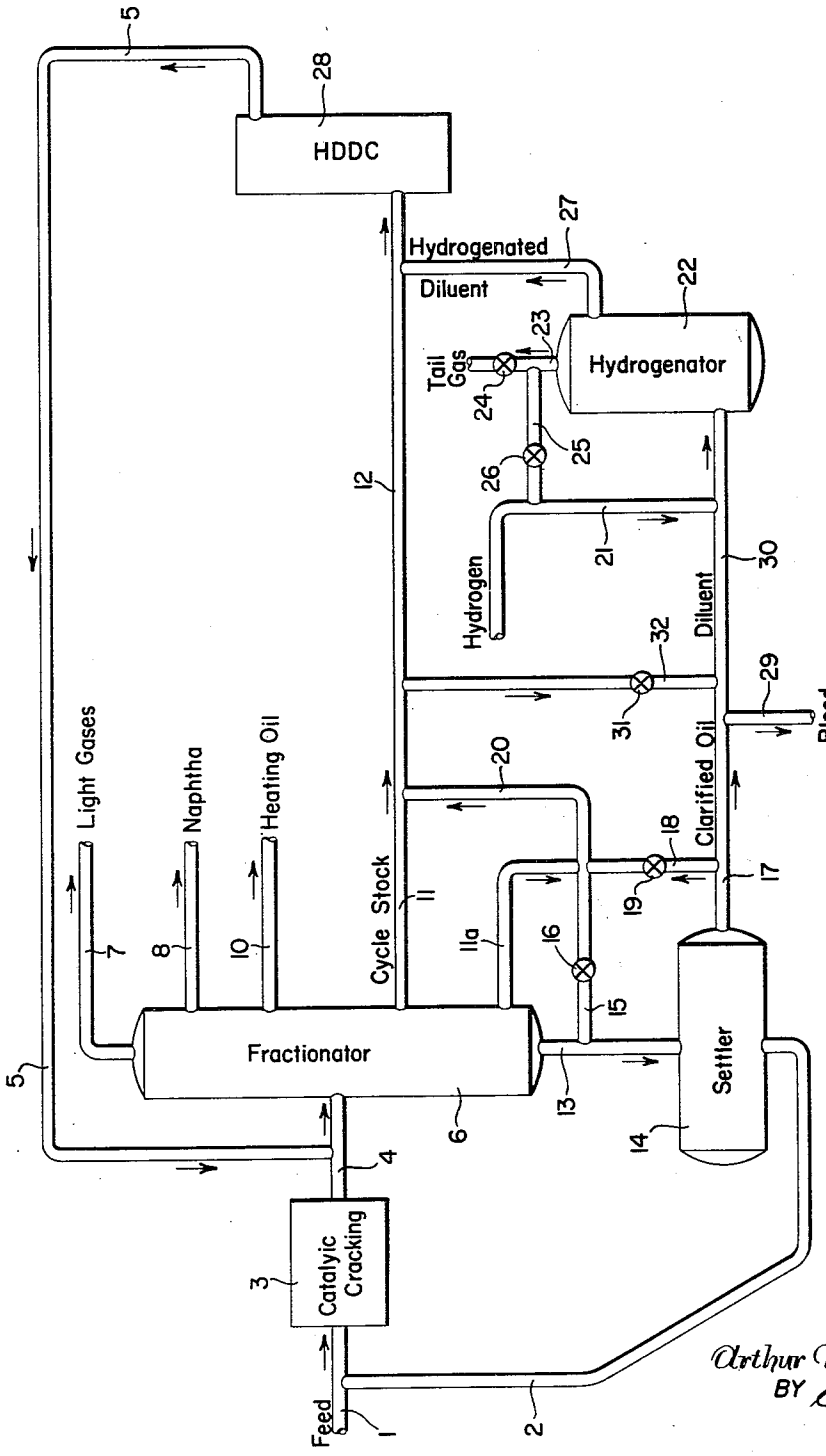
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PROCESS FOR HYDROGENATING AND CRACKING PETROLEUM OILS

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PROCESS FOR HYDROGENATING AND CRACKING PETROLEUM OILS

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The present invention relates generally to the conversion of hydrocarbon oils by catalysis and particularly to a process and a system for converting heavy oils such as gas oils to lighter and more valuble products by a combination of catalytic cracking and hydrogen donor diluent cracking.

The art of catalytic cracking of hydrocarbons is well known. Although catalytic cracking is used in and forms a part of this invention, no elaborate presentation of the technique of catalytic cracking will be made in describing this invention for the above reason.

Recently a process termed hydrogen donor diluent cracking (HDDC) has been proposed. In this process an oil is upgraded by admixing it with a hydrogen donor diluent material, aromatic in nature, and cracking the mixture either thermally or catalytically. The donor diluent is a material such as a thermal tar boiling in the range of 700° to 900° F. having the ability to take up hydrogen in a hydrogenation zone and readily release it in the thermal cracking zone. The donor material is partially hydrogenated by conventional methods using, preferably, a sulphur insensitive catalyst like molybenum sulfide. In this manner of hydrocracking of oils, the oil being upgraded is not contacted directly with the catalyst and does not, therefore, impair its activity by contamination. The amount of concomitant light gases and coke produced by this process is extremely small, usually being about 5 to 10%. The technique of HDDC is more fully presented by co-pending application, entitled, "Upgrading of Heavy Hydrocarbon Oils," by Langer, et al., S. N. 365,335, filed on July 1, 1953.

Co-pending application entitled, "Conversion of Residual Oil Fractions" by Langer et al., S. N. 365,338, filed on July 1, 1953, points out that a partially hydrogenated hydrogen donordiluent can be effectively used in a hydrocracking process to produce good yield of motor fuel or gasoline of a relatively high octane number from heavy residual stocks. It discloses that by adding 5 to 200% by volume of a partially hydrogenated diluent material to a residual oil feed and passing the mixture over a dehydrogenating or hydroforming catalyst, for example, molybdenum oxide on silica-alumina, the feed can be upgraded, even if highly aromatic in nature.

This invention, by the novel application of the above methods of thermal or catalytic hydrogen donor diluent cracking to the material boiling above the gasoline range from a conventional catalytic cracking process, presents a method of catalytically upgrading hydrocarbon oils that is more efficient than those previously suggested.

Accordingly, a major object of the present invention is to convert hydrocarbon oils boiling above 400° F. to lighter, more valuable hydrocarbons such as gasoline. A further object is to catalytically treat oils, such as gas oils or heating oils and to upgrade them to motor fuels with substantially no production of residual fuels or waste materials. Further objects and advantages will appear more fully as the attached drawing, depicting schematically a preferred embodiment of the invention and forming a part of this specification, is discussed in detail.

Generally, the objects of this invention are attained by catalytically cracking a hydrocarbon feed in a conventional manner, separating the product gases to obtain light gases, naphthas, a plurality of gas oil fractions, cycle stock and a bottoms slurry, partially hydrogenating a portion of a heavy fraction (hereinafter referred to as diluent) cracking the cycle stock admixed with the partially hydrogenated diluent and returning the cracked mixture to the same product recovery system used by the catalytic unit. In this manner, the cycle stock is cracked to extinction in the HDDC unit. As before mentioned, the HDDC unit can operate either thermally or catalytically. Alternately, the bottoms slurry from the recovery system (or the clarifier oil therefrom) can be admixed with the cycle stock for the HDDC treatment.

It is readily apparent that this invention offers the following advantages for the upgrading of hydrocarbons over the separate use of either catalytic cracking or HDDC:

1. The hydrogen donor diluent is used only for the cycle stock cracking rather than for the feed stock, thereby reducing the diluent requirement.

2. Limiting the diluent cracking unit to cycle stock feed results in efficient use of the diluent since catalytically cracked cycle stock contains little olefinic or paraffinic material which would consume hydrogen unnecessarily. That is, consumption of hydrogen from the diluent by olefins or paraffins does not improve product quality and would increase the amount of diluent required.

3. Because the hydrogen content of catalytically cracked cycle stock is lower than that of conventional feed to the cracking process, the cycle stock is cracked most advantageously by HDDC.

4. By using the same product recovery system for both units, greater economies are obtained.

5. Very little low value residual material is produced because the heavy ends are treated essentially to extinction.

Referring now to the accompanying drawing, the feed, such as a virgin gas oil boiling from 550° to 1050° F., enters the process through line **1** and is admixed with the recovered catalyst slurry, supplied by line **2**. The mixture is passed to a catalytic cracking unit **3**, here assumed to be a conventional fluid unit with a catalyst regeneration system. Typical cracking conditions for a silica-alumina catalyst of 0 to 200 microns at 50 to 60% 430° F. conversion are: temperature 850–950° F., superficial vapor velocity 1–3 ft./sec., catalyst to oil ratio: 10, feed rate, 1.47 w./hr./w., and pressure 10–20 p. s. i. g. The effluent from the catalytic unit **3** is transferred by line **4** to a separation system, here shown to be a fractionator **6** and a settler or Dorr thickener **14**. A simple separation system is here shown for the purpose of illustration but a more elaborate separation could be used as desired. As portrayed, light gases (C_4-) are removed from the fractionator by line **7** and sent to other processes, such as light ends recovery unit, not shown. The desired naphtha or gasoline fraction (C_4—430° F.) is removed via line **8**, and one or more heating oil fractions (430 to 650° F.) via line **10**. Cycle stock (650°–800° F.) is taken off by lines **11** and **11***a* and passed by lines **20** and **12** to the HDDC unit. The bottoms boiling above 800° F. are passed by line **13** to the settler **14**.

It is to be understood that the temperature ranges of the various fractionator streams can be varied to meet the needs of individual processes. Clarified oil is here used as the source of the donor diluent. It contains higher boiling, larger condensed ring structures and will be partly cracked along with the cycle stock. The clari-

fier oil is used as the example because the purpose of the example is to eliminate high boiling materials or residua. It is to be emphasized, however, that the diluent stream can consist of any catalytically cracked material boiling above 400° F., preferably above 650° F., and including clarified oil, depending upon the demands of specific processes. A separate diluent and cycle stock fractionation could be made but is not mandatory. A single cycle stock selection could be made and a portion of the cycle oil could be partially hydrogenated to yield the donor diluent. This alternate is shown by line **32** and valve **31** which can be used to transfer a portion of the cycle oil or gas oil to the hydrogenator. Provision is also made to process the slurry oil and clarifier oil by HDDC. A portion or all of the slurry oil can be passed from line **13** by line **15** and valve **16** to the cycle stock stream. Also, a portion or all of the clarifier oil, removed from settler by line **17**, can be sent to the HDDC unit by line **18**, valve **19**, lines **20** and **12**. Ordinarily the catalyst suspension in line **13** is concentrated in the settler **14**. The concentrated catalyst suspension is then transferred to the catalytic unit by line **2** and the clarified oil is removed by line **17** and transferred to a hydrogenator **22** by line **30** to serve as the diluent. With high ash feed stocks, it may be necessary to bleed a small amount of clarified oil through line **29** to prevent build up of contaminants in the systems.

About 200 to 6000 s. c. f. of hydrogen per bbl. of diluent is admixed by line **21** with the diluent in line **30** and the mixture is passed over a hydrogenation catalyst in vessel **22**. Conventional operating conditions are contemplated such as a temperature of 650° F., feed rate of 0.1 to 2.0 w./hr./w. and a pressure of 100 to 1000 p. s. i. g. The conditions, in any case, should be so chosen that the diluent is only partially hydrogenated for it has been found that complete hydrogenation greatly reduces the effectiveness of a donor-diluent. 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 naphthenes. The unreacted hydrogen is passed overhead by line **23** and valve **24**. It may be desired to recycle some of this tail gas to line **21** by lines **25** and valve **26**.

The hydrogen donor diluent is passed from the hydrogenator **22** to the cycle stock in line **12** by line **27**. The ratio will depend upon the degree of hydrogenation of the donor, the quality of the cycle stock and the HDDC conditions, but generally it will be about 0.1 to 4 volumes of diluent per volume of cycle stock, preferably 0.2 to 2 volumes. The mixture is then passed to the HDDC unit **28**.

For thermal HDDC, a coil alone or a coil and drum arrangement is used. The temperature of operation is about 750° to 1000° F. with a pressure of 0 to 1000 p. s. i. g. The residence time may vary from ¼ to 5 hours, or the feed rate may be of 0.1 to 15 v./v./hr.

For catalytic HDDC, vessel **28** is filled with a dehydrogenating or hydrogen transfer catalyst such as activated carbon, nickel sulfide, cobalt molybdate or molybdenum oxide on silica-alumina. In the catalytic HDDC operation reaction conditions are (*a*) temperature—700 to 1000° F., (*b*) feed rate of 0.1 to 15 v./v./hr. and (*c*) pressure of 0 to 1000 p. s. i. g.

After this treatment, the product from the HDDC unit is transferred by line **5** to the fractionating column **6**. The following Table I lists the preferred operating conditions for the process of this invention and presents a material balance.

Table I

Fluid catalytic unit:	
Catalyst	silica alumina.
Temperature	900° F.
Pressure	16 p. s. i. g.
Oil inlet temperature	800° F.
Feed rate	2.4 w./hr./w.
Catalyst/oil ratio	12.5.
Hydrogenating unit:	
Catalyst (3/16" pills)	nickel tungsten sulfide.
Temperature	650° F.
Pressure	500 p. s. i. g.
Throughput	0.25 v./v./hr.
HDDC unit (non-catalytic, coil and drum):	
Temperature	900° F.
Pressure	1000 p. s. i. g.
Throughput	2 v./v./hr.
Starting material (Virgin West Texas oil 550°–1050° F. 23.8 API):	
Hydrogen consumed	50 s. c. f./bbl. of feed.
Products, percent on feed:	
C_3—	9.0 wt. percent.
Naphtha, C_4–430	77.1 vol. percent.
Gas oil, 430–600° F.	24.2 vol. percent.
Clarifier oil	0.06 vol. percent.

It is to be understood that this invention is capable of many modifications and is not to be limited by the foregoing example but only by the following claims.

What is claimed is:

1. A hydrocarbon oil conversion process which comprises catalytically cracking a virgin gas oil, separating the cracked product in a separation zone to obtain product hydrocarbons and material boiling above 400° F., partially hydrogenating a portion of said material boiling above 400° F., recombining the hydrogenated portion with another portion of said material boiling above 400° F., converting the recombined mixture in liquid phase under hydrogen donor diluent cracking conditions in the absence of a catalyst, and returning the converted mixture to said separation zone.

2. The process of claim 1 wherein said cracked product is separated to obtain a 650 to 800° F. fraction, and a clarified oil boiling above 800° F., said clarified oil being partially hydrogenated and combined with said 650 to 800° F. fraction to obtain said recombined mixture.

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