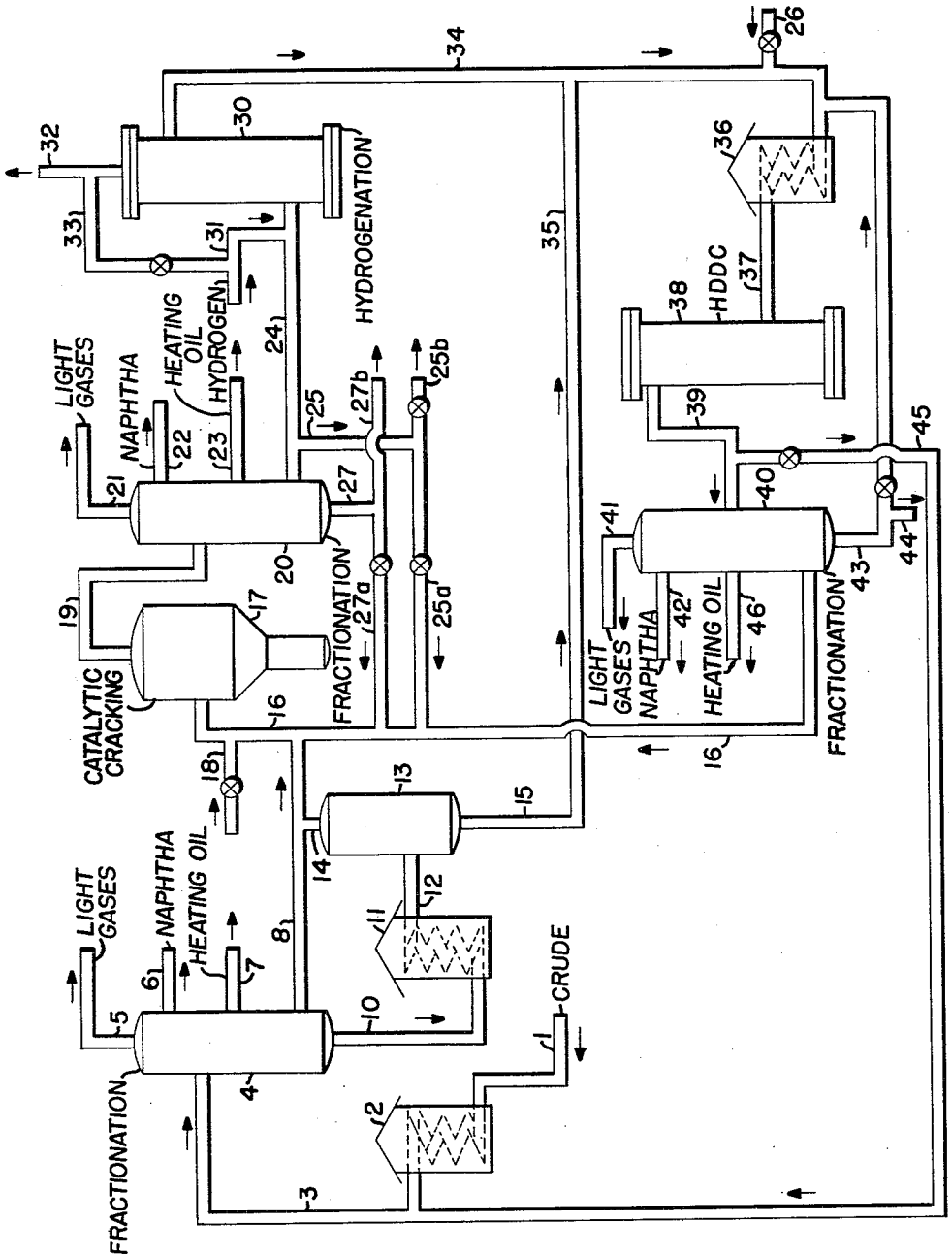
Nov. 27, 1956 H. G. M. FISCHER 2,772,213

HYDROCARBON OIL CONVERSION PROCESS BY CATALYSIS AND HYDROGEN DONOR DILUENT NON-CATALYTIC CRACKING

Filed June 11, 1954



Herbert G. M. Fischer Inventor

By L. Chasan Attorney

United States Patent Office 2,772,213 Patented Nov. 27, 1956

2,772,213

HYDROCARBON OIL CONVERSION PROCESS BY CATALYSIS AND HYDROGEN DONOR DILUENT NON-CATALYTIC CRACKING

Herbert G. M. Fischer, Westfield, N. J., assignor to Esso Research and Engineering Company, a corporation of Delaware

Application June 11, 1954, Serial No. 435,993
5 Claims. (Cl. 196—49)

The present invention relates generally to the conversion of hydrocarbon oils. It pertains particularly to a process and a system for converting heavy petroleum oils to lighter and more valuable products by catalysis and hydrogen donor diluent cracking.

Recently a process termed hydrogen donor diluent cracking (HDDC) has been proposed. In this process, heavy oil is upgraded by admixing it with a hydrogen donor diluent material that contains aromatic-naphthenic constituents, and thermally cracking the mixture. The donor diluent is a material such as a thermal tar boiling in the range of, preferably, 650° to 1000° 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 sulfur insensitive catalyst like molybdenum 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 relatively small, usually being in the order of about 5 to 10%. This technique of HDDC is more fully depicted in copending application, entitled, "Upgrading of Heavy Hydrocarbon Oils," by Langer et al., S. N. 365,335, filed on July 1, 1953.

The present invention, by application of the above method of hydrogen donor diluent cracking to heavy, low value hydrocarbons such as vacuum residua, tars, asphalts, etc., and by selection of a catalytic cycle stock as a source of hydrogen donor diluent, proposes an attractive combination process heretofore unappreciated. By use of a normally surplusage catalytic cycle stock as the donor diluent and by specific processing sequences, the HDDC process is advantageously integrated with catalytic cracking processes to yield a highly efficient petroleum oil conversion process.

It is, accordingly, a major object of the present invention to convert hydrocarbon oils, particularly heavy petroleum oils boiling above about 1000° F., to lighter, more valuable compounds. Another object is to develop a method for processing petroleum oils typified by a minimum production of degradation products, e. g., light gases and coke. A specific object is to propound a process for upgrading hydrocarbon oils having as essential features the steps of catalytic cracking and hydrogen donor diluent cracking of selected fractions of the oils. Further objects and advantages will appear more clearly as the attached drawing, depicting schematically a preferred embodiment of the invention and forming a part of this specification, is discussed in detail.

The attached drawing illustrates diagrammatically a preferred process adapted to achieve the objects of this invention.

Generally the objects of this invention are obtained by catalytically cracking selected gas oils to obtain products of high quality and heavy cycle stocks and partially hydrogenating a portion or all of the heavy cycle stocks. The hydrogenated cycle stock is then blended with a hydrogen deficient material such as a vacuum residuum and the resulting mixture is thermally treated or cracked to obtain naphthas and light and heavy thermal gas oils.

The heavy thermal gas oil is recycled to the catalytic cracking unit as an improved catalytic cracking feed stock.

Specifically, the advantages of this invention are achieved by thermally cracking a high boiling residuum while it is diluted with a partially hydrogenated selected cycle stock from a catalytic cracking unit. The hydrogenated cycle stock transfers hydrogen during the thermal cracking to the residuum, thereby upgrading it and, because not all of the hydrogen introduced into the cycle stock is transferred, the cycle stock is upgraded by the residual hydrogen remaining after the HDDC treatment, and is an improved catalytic cracking feed stock.

This invention proposes a processing sequence in which a suitable fraction of catalytic cycle stock, preferably a fraction boiling in the range of 650° to 1000° F., is hydrogenated for use as a donor diluent during thermal cracking of petroleum residua. For optimum operation, as much hydrogen as possible is introduced into the diluent short of reducing its activity by complete hydrogenation of the polynuclear aromatics to naphthenes. This diluent is blended with residuum using as high a diluent concentration as possible consistent with the relative volumes of cycle stock and residuum available. After thermal cracking or treatment, the recovered diluent fraction, e. g., material boiling above about 650° F., is returned to catalytic cracking as an improved cycle stock rather than regenerated and returned to the donor diluent cracking stage as is customary in normal HDDC operations.

As is known by the art, as the aromatic to naphthene ratio of a catalytic feed stock increases, cracking quality decreases. In the present invention, the residual hydrogen remaining in the cycle stock after HDDC serves to improve the quality of the cycle stock as a catalytic cracking charging stock by substantially decreasing its aromatic to naphthenic ratio.

Although the present invention is applicable to any type of crude oil, distillate or residual fractions therefrom, or mixtures thereof, it is most advantageously applied to the processing and converting of crudes that normally yield high percentages of residual fractions. As will be seen, in the practice of this invention, each fraction of an oil is selectively processed under conditions designed to secure optimum yields of motor gasolines and of middle distillates suitable for fuels for home or industrial heating, for use in diesel engines or gas turbines, etc.

For convenience, the pertinent operating conditions applicable to the following example are summarized in Table I. Referring now to the drawing, a crude enters the process by line 1, is heated in furnace 2 to a suitable temperature, and transferred to an atmospheric fractionation column 4 by line 3. Light gases are removed from the column overhead by line 5, a naphtha fraction and a heating oil fraction are removed by lines 6 and 7 respectively. Line 8 removes a gas oil fraction, boiling in the range of about 650° to 900° F. and designated as feed for catalytic cracking. The naphtha, heating oil and gas oil fractions can, of course, be further processed by conventional methods such as hydrofining, stabilization, blending, etc., to obtain commercially salable products.

Advantageously, the heavy portion of the naphtha can be subjected to processes such as hydroforming to increase the quality and octane rating of the gasoline product and to, concurrently, produce hydrogen. This hydrogen can then be used to hydrogenate the diluent, as is hereinafter described. With proper selection of operating conditions and feed stocks, the process, including the hydroforming step, may be made to be substantially balanced as to hydrogen production and consumption. If a crude source does not, however, supply a sufficient amount of hydrogen, then extraneous hydrogen is used.

Line 10 removes the residuum from the fractionation

tower and transfers it to a furnace **11** wherein it is reheated to a suitable temperature for further separation. From the furnace, the residuum is transferred by line **12** to a vacuum distillation unit **13**. Further gas oils are removed from the residuum by the vacuum distillation and are blended with the material in line **8** by line **14**. Heavy vacuum residuum boiling above about 1000° F. is removed from the vacuum tower by line **15**. It is to be appreciated that in certain applications, there will be no need or justification for a vacuum distillation unit. In such a case, the atmospheric bottoms can be transferred to the HDDC unit.

The gas oil in line **8** is mixed with thermal gas oil, obtained as hereinafter described, in line **16** and passed to a catalytic cracking unit **17**. If desired, other catalytic cracking feed stocks may be admitted to the process by line **18**. Suitable tankage may be interposed at this point to collect and blend these various feed streams to the catalytic cracking unit to add operating stability to the process.

Any conventional catalytic process is suitable for the purpose of this invention. Such a catalytic process may have a fluid bed, a fixed bed or a gravitating type of bed. A fluidized catalyst bed reactor with a fluid bed regenerator (not shown) is preferred and is used as the catalytic process in this example. The effluent from the catalytic cracking unit is transferred to a fractionation column **20** by line **19**. Lines **21**, **22** and **23** remove light gases, naphthas and heating oils respectively, from column **20** as products of the process. Line **24** removes a cycle stock boiling in the range of about 650° to 1000° F. and designated as feed to a hydrogenation unit **30**. In some instances it may not be necessary to hydrogenate all the cycle stock to serve as a diluent during HDDC. Thus, lines **25** and **25***a* may be used to recycle a portion of this cycle stock to the catalytic cracking unit. A portion or all of the excess cycle stock may be removed from the process as product by lines **25** and **25***b*.

Broadly, any material boiling above the gasoline range from the catalytic cracking unit will serve as a hydrogen donor diluent after partial hydrogenation. In certain applications or with particular feed stocks, it may be desired to use as a hydrogen donor diluent fractions boiling above the preferred diluent boiling range in order to maintain heat and material balances and/or to obtain optimum product distributions. It is to be understood that although the preferred donor diluent boiling range is from about 650° to 1000° F., other diluent boiling ranges can be satisfactorily used. For example, when heart cut recycle catalytic cracking is practiced, the diluent boiling range can be 900° to 1050° F. It should be noted that as the boiling point of a selected diluent increases, its aromaticity will increase and thus its ability to take up and to transfer hydrogen will increase.

Bottoms are removed from fractionator **20** by line **27**. Although it is not shown, a separation step can be incorporated at this point to concentrate the catalytic solids remaining in the bottoms, as is customary in some processes. However, it is known to operate a catalytic cracking process without such a separation step. A portion of the bottoms, or slurry oil, if a separation step be used, may be recycled to the cracking unit by line **27***a*. It is desirable to remove by line **27***b* a portion of the bottoms as purge to prevent an excessive build-up of contaminants in the system.

Generally, a petroleum oil process can consume roughly about 8–10% of the material processed as fuel to supply heat. As the process of this invention minimizes the amount of degradation and low value products produced, this process can be made to be substantially balanced as to fuel requirements. The light gases produced will serve as a heat source and further amounts of fuel can be obtained by purges of the heavy bottoms or residual fractions. The extent of the purges can be regulated to balance the heating demands of the process and heavy oils existing beyond this requirement can be recycled substantially to extinction.

The material to be hydrogenated is transferred to a hydrogenation unit **30** which is supplied by line **31** with hydrogen from a source not shown. Conventional operating conditions are used during the hydrogenation and it is preferred to use a relatively sulfur insensitive catalyst such as molybdenum sulfide or cobalt molybdate. Line **32** removes tail gases from the hydrogenator, a portion of which may be recycled by line **33**.

The conditions are so chosen that the diluent is only partially hydrogenated for it has been found that complete hydrogenation greatly reduces the effectiveness of the 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. However, the degree of hydrogenation used in this invention is generally higher than that normally used in HDDC operations.

The partially hydrogenated donor diluent is transferred via line **34** to the HDDC unit **38**. The hydrogen-deficient material to be upgraded is supplied to the unit by line **35**. This hydrogen deficient material will be composed primarily of the vacuum residuum supplied by line **15**. However, it may be desired in some applications to also subject other low value materials to HDDC. These can be admitted to the process by line **26**. The relative proportions of diluent and residuum used will depend upon the degree of hydrogenation of the diluent, the amounts of the materials available and like factors.

The resulting mixture is passed to furnace **36**, wherein it is heated to a conventional thermal cracking temperature, e. g., 750° to 1000° F. under a pressure to maintain the mixture substantially in the liquid state. From the furnace, the heated mixture is transferred by line **37** to a soaking or time drum **38**, wherein the mixture is held for a sufficient period of time to allow the cracking and hydrogen exchange to take place to the degree desired. In some cases, such as in vis-breaking type operations, a soaking drum may not be required.

After the thermal cracking, the cracked mixture is transferred to a fractionation tower **40** by line **39**. Light gases are removed overhead from the tower by line **41** and a naphtha fraction is removed by line **42** to further processing, not shown. A heating oil fraction is removed by line **46** as product. Line **16** transfers material boiling in the gas oil range to the catalytic cracking unit. Because of the HDDC treatment, the gas oil is lower in sulfur content, in aromatic content and in unsaturation, and has a higher hydrogen to carbon ratio and is particularly suitable as a charging stock to the catalytic cracking unit. Bottoms boiling above about 1000° F. are removed from fractionator **40** by line **43**, a major portion of which may be recycled for further treatment. It is desirable, however, to purge or bleed off a portion of the contents of line **43** by line **44** in order to prevent excessive build-up of contaminants in the system and to provide fuel to the process.

An attractive alternative processing scheme is to pass the product from the HDDC unit directly to fractionator **4** by lines **39**, **45** and **3** to be separated therein whereby fractionator **40** is eliminated.

To further elucidate this example, Table I summarizes operating conditions pertinent to the present invention and presents a specific example of operating conditions. Example 1 of Table II lists the products obtainable by operating a process, similar to that depicted in the drawing, in accordance with the example of Table I when the feed stock has the inspections listed. Example 2 of Table II lists the products obtainable from the same feed stock when conventional processing techniques are used, e. g., primary fractionation, vacuum distillation, and catalytic cracking of the virgin gas oil with heart cut recycle. By comparison of the two examples, the advantages obtainable by practice of the present invention are readily

apparent. It can be seen that this invention results in a 95% decrease in the amount of residual oil produced.

TABLE I

	Range	Example
Catalytic Cracking Conditions, Fluid Unit:		
Catalyst		Silica Alumina.
Temperature, °F	850 to 1,000	930.
Pressure, p. s. i. g	0 to 50	10.
Feed Rate, W./Hr./W	0.5 to 3	1.7.
Catalyst/oil ratio		9.2.
430° F. Conversion per pass Vol. percent [1].	50 to 80	72.5.
Hydrogenation Conditions:		
Catalyst		Nickel Tungsten Sulfide.
Temperature, °F	600 to 750	650.
Pressure, p. s. i. g	100 to 1,000	500.
Throughput, V./V./hr.	0.1 to 2	0.25.
H_2 Consumed, S. C. F./bbl. diluent.	200 to 2,000	500.
HDDC Conditions (Coil and/or Drum):		
Temperature, °F	above 750	900.
Pressure, p. s. i. g	50 to 2,000	400.
Throughput, V./V./hr.	0.5 to 10	4.
Diluent/Oil Ratio	0.25 to 2	1.2.
Diluent Boiling Range, °F.	650° F. and above.	650 to 1,000.
430° F. Conversion per pass, Vol. percent [1].	30 to 80	45.8.

[1] 430° F. Conversion is defined as: 100 vol. percent feed—vol. percent products boiling above 430° F., based on fresh feed.

TABLE II

Feed Stock—Bachaquero Crude:

API gravity	14.1
Sulfur, wt. percent	2.60
Vis. @ 122° F. SF	187
Salt content lb./M. B	7
Pour, ° F	+10
Flash, ° F	+80

	Example 1	Example 2
Products, percent based on Feed:		
Light Gas, C_3-, Wt. percent—		
Atmospheric fractionator	0.1	0.1
Catalytic Unit fractionator	4.6	3.7
HDDC Unit fractionator	2.5	
Total	7.2	3.8
Naphtha, C_4-430° F., Vol. percent—		
Virgin	7.5	7.5
Catalytic	25.3	19.9
HDDC	19.4	
Total	52.2	27.4
Heating Oil, 430°-650° F., Vol. percent—		
Virgin	17.5	17.5
Catalytic	11.2	8.8
HDDC	16.7	
Total	45.4	26.3
1,000° F.+Bottoms (Inc. Bleeds), Vol. percent—		
Catalytic (Heavy Cycle Stock)	1.1	0.9
HDDC	0.9	
Vacuum		41
Total	2.0	41.9
Coke (including catalytic carbon)	8.5	6.6
Internal Flows, Vol. percent based on feed:		
Gas Oils to Catalytic Unit, 650° to 1,000° F.—		
Source: Virgin	34.5	
HDDC Unit	[1] 50.9	
Total	85.4	
Diluent to Hydrogenator, 650° to 1,000° F	48	
Vacuum residuum to HDDC Unit, 1,000° F.+	41	
Total	89	

[1] Includes diluent recycled.

Although the above example depicts the present process as initiating with the separation of a whole crude, the process is not limited thereby. The catalytic cracking charging stock can originate from any convenient source and the hydrogen deficient material upgraded in the HDDC unit can include tars, asphalts, extracts, shale oils, coal tars, pitches, whole crudes, residual and distillate fractions therefrom, or mixtures thereof.

Having described the invention, what is sought to l protected by Letters Patent is succinctly set forth in tl following claims.

What is claimed is:

1. A process for converting hydrocarbon oils whic comprises catalytically cracking heavy distillate oils i a catalytic cracking zone under catalytic cracking co ditions, separating from the effluent therefrom a cyc stock, partially hydrogenating said cycle stock in a h drogenation zone under hydrogenation conditions to ol tain a hydrogen donor diluent, admixing said hydroge donor diluent with a relatively high boiling heavy oi cracking the mixture in a thermal treating zone und non-catalytic hydrogen donor diluent cracking cond tions, separating from the thermally treated mixtu thermal gas oils including spent hydrogen donor dilue and passing said thermal gas oils to said catalytic crac ing zone to form at least a portion of said heavy distilla oils.

2. A process for upgrading hydrocarbon oils compri ing catalytically cracking a petroleum oil boiling in th range of 650° to 1000° F. in a catalytic cracking zon separating the effluent therefrom into at least produ fractions boiling in the naphtha and heating oil range a cycle stock fraction boiling in the range within th limits of 650° to 1000° F. and bottoms boiling abo 1000° F., partially hydrogenating at least a portion said cycle stock in a hydrogenation zone, to obtain hydrogen donor diluent, admixing said hydrogen don diluent with a hydrogen deficient oil boiling above abo 1000° F. in a proportion in the range of 0.25 to 2 vo umes diluent/volume of oil, thermally treating the r sulting mixture at a temperature above 750° F. in non-catalytic thermal cracking zone, separating from th effluent from said thermal cracking zone into furth product hydrocarbons and a recycle fraction includi spent hydrogen donor diluent boiling in the range about 650° to 1000° F., and returning said recycle fra tion to said catalytic cracking zone to be treated there along with the said petroleum oil.

3. The process of claim 2 wherein said petroleu oil boiling above about 1000° F. comprises a vacuu residuum and a bottoms fraction obtained from the e fluent from said thermal cracking zone.

4. A method of processing petroleum oils which con prises separating a crude oil into at least product hydr carbons, gas oils and residuum boiling above about 1000 F., catalytically cracking at least a portion of said ga oils along with a thermal cycle stock, obtained as her inafter described, separating the catalytically cracked o into at least further product hydrocarbons, catalytic cyc stock and bottoms, partially hydrogenating at least portion of said catalytic cycle stock, admixing the h drogenated material with said residuum, thermally crac ing the resulting mixture at a treating temperature abo 750° F., under non-catalytic hydrogen donor dilue cracking conditions, separating the thermally cracke mixture into at least a still further product hydrocarbon thermal cycle stock which includes partially dehydr genated products from said hydrogenated material an residue, and recycling and admixing said thermal cyc stock with said portion of gas oils to be catalyticall cracked therewith.

5. The process of claim 4 when said thermally cracke mixture is admixed with said crude oil and the resultin mixture is separated in a common separation zone.

References Cited in the file of this patent

UNITED STATES PATENTS

2,426,929	Greensfelder	Sept. 2, 194
2,459,465	Smith	Jan. 18, 194
2,467,920	Voge et al.	Apr. 19, 194
2,620,293	Blue et al.	Dec. 2, 195