Nov. 27, 1956 J. STEWART ET AL 2,772,222

PROCESS FOR CRACKING GAS OILS TO GASOLINE

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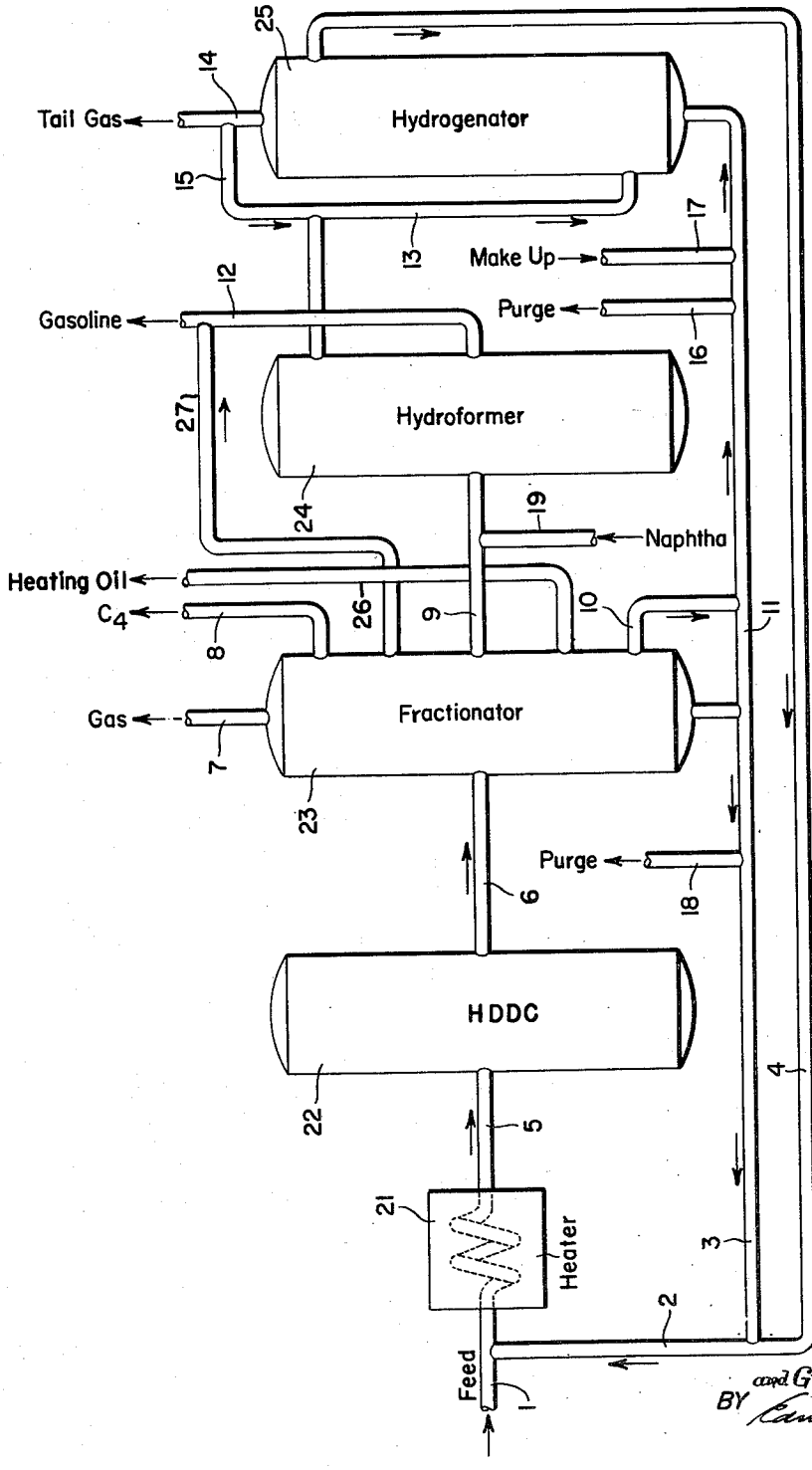


Fig. 1.

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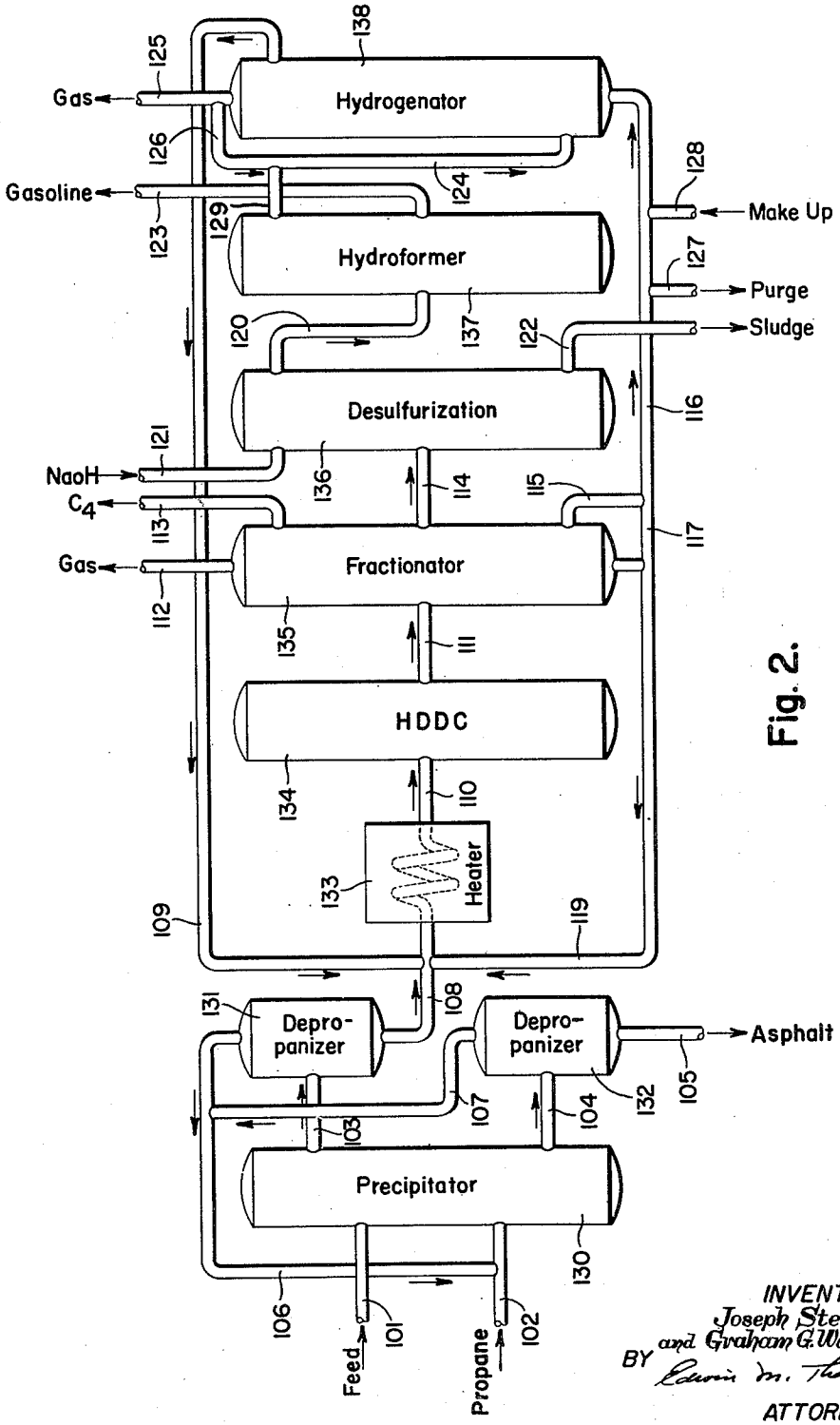


Fig. 2.

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PROCESS FOR CRACKING GAS OILS TO GASOLINE

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3 Claims. (Cl. 196—50)

The present invention relates to the upgrading of hydrocarbon oils to produce lighter and more valuable oils. It pertains particularly to an improved process for hydrogenating and upgrading gas oils, catalytic cycle oils or deasphalted oils boiling above the gasoline end point to the more economically desired gasolines.

Catalytic cracking of gas oils and the like has been practiced for many years to produce gasoline. While catalytic cracking has proved immeasurably valuable and has been much used as a means of satisfying the demand for high octane gasoline, it still is today a relatively expensive process and is so because of inherent limitations. There must be regeneration of the catalyst because of poisoning and carbon deposition. There must be replenishment of the catalyst because of losses by attrition and failure of complete separation from products. The initial capital investments and operating costs for such a plant are usually high. It is apparent, therefore, that if a process can be developed that can produce the same or nearly the same results as a catalytic unit for the same feed stock and does not involve the high initial costs or the high operating costs of the catalytic unit, then such a process would be of considerable economic importance. This invention makes possible a process that will obviate the necessity, in certain instances, of catalytic cracking of materials like gas oils in order to upgrade them. This invention is based on the discovery that it is possible to substitute hydrogen donor diluent cracking (HDDC) for catalytic cracking in the process of upgrading gas oils when the gasoline produced is hydroformed.

The primary object of the present invention is to make possible the conversion of all, or substantially all, of a hydrocarbon material in the nature of gas oil to more valuable gasolines. Another object is to present a process that is more economically desirable than the present method of producing high octane gasolines. Another more specific object is to supplant the use of catalytic cracking steps in the process of upgrading hydrocarbons. A further specific object is to provide a method to thermally upgrade oil stocks to gasolines when the gasoline produced is hydroformed. Further objects and advantages will appear more clearly as this description proceeds. Reference will be made to specific embodiments illustrated diagrammatically in the attached drawings which form part of the specification.

In the drawing—

Figure 1 illustrates schematically the invention as applied to the upgrading of a clear gas oil;

Figure 2 illustrates diagrammatically the process as it is used to convert an oil requiring deasphalting.

Generally the process of this invention is carried out by mixing the gas oil feed with a recycled partially hydrogenated oil fraction, boiling in the range of 400° to 950° F., which acts as a hydrogen donor. This donor contains a substantial proportion of partially, but not completely, hydrogenated polynuclear aromatic compounds. After this treatment the material is fractionated to obtain gaseous hydrocarbons, gasoline, a diluent cut and heavy

bottoms. The gasoline fraction is hydroformed thereby increasing its octane rating and producing hydrogen. The diluent cut is hydrogenated in the presence of a suitable catalyst using the hydrogen created in the hydroforming step. The process can be so operated so as to produce or consume hydrogen as may be desired. The hydrogenated diluent, along with the heavy bottoms, is then recycled to the hydrogen donor diluent cracking step.

A co-pending application, "Upgrading of Hydrocarbon Oils," Ser. No. 365,335, filed July 1, 1953, by Arthur W. Langer, Jr., now abandoned, discloses the nature of the hydrogen donor diluents and their utility in the conversion of heavy petroleum stocks to lighter, more valuable distillate. The above application points out that it is not necessary to use substantially pure organic compounds as the donor diluent but that heavy thermal tars make superior and inexpensive diluents. It further points out that incomplete hydrogenation of the tars is much more efficient to effect conversion, i. e., to hydrogenate petroleum compounds. This invention is predicated upon the use of such a donor diluent. By this invention the conversion of relatively light petroleum fractions to lower boiling gasolines or naphthas is effected without the use of extraneous and expensive hydrogen. This hydrogen balance is obtained by removing hydrogen from the naphthas, produced by HDDC, by hydroforming, thus producing a high octane gasoline, and concurrently reintroducing the hydrogen by means of a donor diluent into the cracking stage thereby avoiding the formation of coke during the cracking.

It is possible according to the present invention to use the HDDC process in place of the catalytic process to convert a gas oil to a gasoline when subsequently the gasoline is hydroformed. The mechanism of this invention can be envisaged by reference to thermal upgrading of oils. Thermal cracking of oils, per se, has never proved practicable to prepare stock for subsequent catalytic reforming because at the temperatures necessary to produce substantial gasoline portions many unsaturates are produced. These unsaturates form gums and tars which render the gasoline unsuitable for commercial use. Catalytically reforming such a gasoline results in high catalyst contamination and the production of relatively valueless products. In the present process the presence of hydrogen donors during thermal cracking prevents the formation of such unsaturates by supplying readily available and easily transferred hydrogen. Thus, the gasoline formed has the desired characteristics for subsequent catalytic reforming.

In order to be effective the removal of hydrogen from the donor must be substantially easier on the average than hydrogen removal from either the aromatic or aliphatic fractions in the oil being converted. Available hydrogen-donor diluent, moreover, must be present in a relatively high concentration so that collision between the free radicals, produced by the heat applied in thermal cracking, with aromatic or aliphatic molecules, is less probable than collision with donor molecules. Moreover the dehydrogenated diluent must be such that it or a good part of it can readily be recovered, rehydrogenated and recycled.

As suggested above, prior art has mistakenly supposed that the more hydrogenated materials make the superior hydrogen donors. This has been proved to be an erroneous and unwarranted assumption. A heavy oil fraction boiling above 500° F. up to about 1200° F., containing substantial and preferably at least major proportions of condensed ring aromatics and having added thereto some easily removable hydrogen atoms, but not enough to aproach saturation, shows outstanding utility as hydrogen donor material. The more highly hydrogenated aromatics show much less activity. Some of the

material suggested by prior investigators such as hydrogenated benzene show no activity at all for the purposes of the invention. Moreover pure or substantially pure compounds or hydrogenated compounds derived from pure compounds are usually relatively very expensive and their use as hydrogen donor diluents is not economically justifiable.

The following data, obtained by comparing the product of an ordinary catalytic process and the process of this invention, will illustrate the utility of this invention.

Table I compares the products from a catalytic cracking process and this process when the material treated is a deasphalted West Texas vacuum residuum. It can be seen that the process of this invention competes favorably with the catalytic cracking process.

TABLE I

Feed·

API gravity	8.0
Aromatic index	47
Naphthene index	6
Diesel index	12.5
Conradson carbon	8

Products	Catalytic Cracking	HDDC+ Hydroforming
C_3-gas, wt. percent	15	7.
Gasoline, vol. percent	44 (94 Res. Octane).	48 (95 Res. Octane).
Heating Oil, vol. percent	20	43.
Cycle Stock, vol. percent	28	3.
Coke, wt. percent	6	0.6.
		(390 S. C. F. H_2/bbl. of feed to cracking stage).

Referring now to the drawings:

In Figure 1, the gas oil to be converted enters through line **1** where it is mixed with recycle bottoms from the fractionator **23** and a hydrogenated diluent from the hydrogenator **25**, the bottoms and the diluent being conveyed by lines **3** and **4** respectively to line **2** which admits them to be mixed with the feed. The gas oil has a preferred boiling range of about 650° to 1000° F., but it may vary anywhere from 430° F. to 1200° F. It may be virgin gas oil or gas oils from coking, thermal or catalytic cracking process. It should be relatively clean and for this reason it may be necessary to deasphaltize the oil. The ratio of mixing the diluent and feed components will vary with the history of the feed, the amount of hydrogenation desired, the quality of the hydrogen donor and many other like factors. The ratio used may be varied from 0.1 to 5.0 volumes diluent per volume of feed but a 0.1 to 1.0 ratio is preferred. The reactants are suitably heated in a heater **21** and then passed via line **5** to the HDDC zone **22** where the hydrogen transfer occurs. As depicted, a coil and drum arrangement is used but any other method of thermal treatment is quite satisfactory. The HDDC or thermal cracking step can be operated under conditions more severe than those used in the residuum process since the feed stock is lighter and there is, therefore, less probability of coking. Suitable operating conditions are about 850°–950° F., 2–5 v./v./hr. and 300–2000 p. s. i. g. By line **6** the reactants are transferred to the fractionator **23** where the products are separated. Gas and a light fraction, e. g., C_4 to C_5 are by lines **7** and **8** respectively removed and may be transferred to other processes such as polymerization or may be consumed as fuel. Preferably, a light naphtha fraction boiling in the range of C_5 to 200° F. is separated and removed by line **27**. It could, however, be hydroformed. A gasoline fraction boiling in the range of 200° to 430° F. is separated and sent to hydroforming unit **24** via line **9**. A heating oil fraction boiling in the range of 430° to 650° F. can be removed by **26** as product as shown or can be recycled to the feed as flux. If necessary, a diluent cut is made. As depicted here, this cut has a boiling range of 650° to 950° F. It is preferred that the diluent have this boiling range but the whole bottoms product can be used as the hydrogen donor if it does not have impurities deleterious to the hydrogenation stage catalyst. Rather than use all the bottoms, a part only may be needed, which could be transferred by line **11**. If the total bottoms are recycled via line **3**, then it may be necessary to purge some of it by line **18** in order to prevent excessive build-up of contaminants. It may be necessary to desulfurize the gasoline before hydroforming but in this illustration that step is not shown. Such desulfurization can be accomplished by any of several known means.

The gasoline is hydroformed under suitable conditions and in the presence of a catalyst. Such conditions may be 750° to 1150° F., 0.5–6.0 w./hr./w. and 50 to 1000 p. s. i. g. The catalyst can be any of several well-known types but preferably a platinum or molybdena catalyst is used. The reformed gasoline produced is removed by line **12** and may be, as is indicated, blended with the C_5–200° F. fraction in line **27**. The hydrogen produced by the hydroformer is passed via line **13** to the hydrogenator where it is used to hydrogenate the donor diluent material.

The amount of hydrogen produced in the hydroforming step can be controlled in part by proper regulation of temperature and proper catalyst selection. However, rather than sacrifice yield, virgin naphtha can be introduced via line **19** to control the hydrogen production. It can readily be seen that by judicious control of temperature, catalyst and virgin naphtha ratio and overall process can be made a balanced, consuming or producing one with respect to hydrogen.

The diluent cut may contain built up impurities and objectionable ingredients which do not contribute to the hydrogen donor diluent function and therefore a purge line **16** is indicated. A make-up line **17** is used to add a suitable diluent to offset the purge and processing losses. This make up tar can be obtained from other processes in a commercial refinery. The diluent is passed to the hydrogenator where it is contacted with the by-product hydrogen from the hydroforming step. As mentioned, the donor diluent should be partially but not fully hydrogenated. Hydrogen should be supplied to the hydrogenator at a rate of about 500 to 2500 s. c. f. per barrel of thermal tar fed to the hydrogenator. The hydrogen, after passing through the hydrogenator, is preferably recycled to the hydrogenator via line **15**. The unit is operated at moderate pressure of the order of 500 p. s. i. g. Conventional temperatures are used and conventional catalysts, preferably of the sulfur insensitive type, such as molybdenum sulfide or nickel-tungsten sulfide are employed. There will be some tail gas produced, removed by line **14**, that can be used in other processes or consumed as fuel.

For the above described process, if the feed amounts to 1000 bbl./day of a virgin gas oil boiling in the range of 900° to 1100° F., the following yields would be expected:

Internal

Recycle diluent, 330 bbl./day, 650° to 900° F. boiling range.
Recycle bottoms, 400 bbl./day, 900+ °F. boiling range.
Hydrogen from hydroformer, 400,000 s. c. f./day.
Gasoline from fractionator, 562 bbl./day, 65° to 430° F., boiling range.

External

Gasoline, 465 bbl./day, 65° to 430° F. boiling range.
Dry gas, 450,000 s. c. f./day.
C_4 fraction, 43 bbl./day.
Tail gas, 11,000 s. c. f./day.
Diluent and bottoms purge 20 bbl./day.

Referring now to Figure 2, a system is shown for converting an asphaltic oil boiling above the gasoline range to lighter and more valuable oils. The feed enters

the process through line **101** and is mixed with propane, furnished by line **102**, in a conventional asphalt precipitator **130**. The conditions and manner of operation for propane deasphalting are well known to the art and need not be recited here. Although a propane precipitator is here shown any other suitable means of deasphalting could be used. The asphaltic phase leaves the precipitator through line **104** and goes to a depropanizer **132** where the propane is separated and recycled through lines **107** and **106** to the precipitator. The asphalt is removed by line **105**. The extract is taken by line **103** to another depropanizer where the separation is effected, the propane being recycled via line **106**. The deasphalted feed is then mixed with the recycled hydrogenated tar, supplied by line **109**, and the recycled bottoms, supplied by line **119**, and fed to a heater **133** by line **108**. The reactants are then conveyed to the HDDC unit **134** by line **110**. The product leaves the unit by line **111** and is separated in fractionator **135**, here simply portrayed. The light gases are removed from the fractionator by line **112**, hydrocarbons boiling below the gasoline range by line **113**, naphtha boiling in the range of 65° to 650° F. by line **114**, a diluent cut, if necessary, boiling in the range of 650° to 900° F. by line **115** and a bottoms fraction by line **119**. Again, if it is desired, all or some of the bottoms can be hydrogenated by passing them through line **117** to the diluent line **116**.

If necessary, the gasoline fraction can now be desulfurized. Any conventional means can be used such as hydrosulfurization, catalytic or extraction methods. Shown on the drawing is a caustic wash. The caustic enters the desulfurizer **136** by line **121**, flows downward countercurrent to the gasoline and leaves by line **122**. After this treatment, the gasoline is passed by line **120** to the hydroformer **137** and after treatment is transferred by line **123** to subsequent blending or stabilization operations (not shown).

The diluent cut from the fractionator is passed by line **116** to the hydrogenator. Hydrogen from the hydroformer is added to the tar via lines **129** and **124**. The hydrogenated tar is recycled to the depropanized feed by line **109**. Hydrogen from the hydrogenator is recycled through lines **126** and **124** or purged as spent gas by line **125**. A diluent purge is made by line **127** and replacement diluent from other refinery processes may be added by line **128**.

The above description and exemplary operations have served to illustrate specific embodiments of the invention. It is to be understood that the invention embraces such other variations and modifications as come within the spirit and scope thereof.

What is claimed is:

1. A hydrogenation and reforming process for converting gas oils to gasolines which comprises: mixing a gas oil feed with 1 to 5 volumes of a hydrogen donor diluent and a recycled bottoms fraction, said hydrogen donor diluent predominantly comprising partially hydrogenated polynuclear aromatics boiling in the range of 650–950 F. derived from a heavy thermal tar; thermally cracking the resulting mixture in the absence of a catalyst at a temperature in the range of 800–1000° F., a residence time in the range of 2–5 v./v./hr. and a pressure in the range of 300–2000 p. s. i. g.; separating the cracked mixture into at least a light fraction boiling below gasoline, gasoline boiling up to about 650° F., a spent diluent fraction boiling in the range of 650–950° F., and a heavy bottoms fraction; hydroforming said gasoline in thepresence of a catalyst at a temperature in the range of 750–1150° F., a residence time in the range of 0.5–6.0 w./hr./w. and a pressure in the range of 50–1000 p. s. i. g., producing thereby a relatively higher octane gasoline product and by-product hydrogen; partially hydrogenating at least a major portion of said spent diluent fraction in the presence of a hydrogenation catalyst with 500–2500 s. c. f. of hydrogen per barrel of spent diluent fraction, a major portion of said hydrogen being composed of said by-product hydrogen; and recycling and blending the partially hydrogenated portion with said feed.

2. The process of claim 1 wherein said gasoline obtained from the thermal cracking step is desulfurized prior to being hydroformed.

3. The process of claim 1 wherein said gas oil feed is obtained from a deasphalting operation.

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