Feb. 27, 1962 F. G. CIAPETTA ET AL **3,023,159**

CONTROLLED HYDROCRACKING PROCESS

Filed March 9, 1956 2 Sheets-Sheet 1

Fig. 1

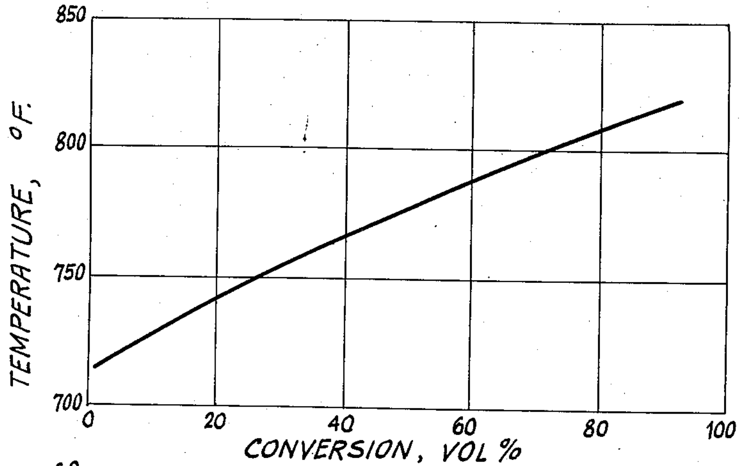


Fig. 2

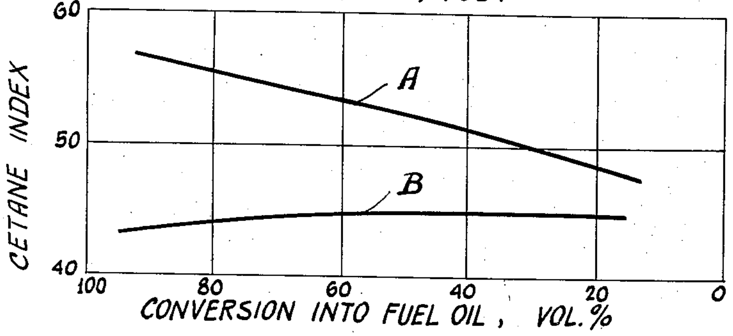
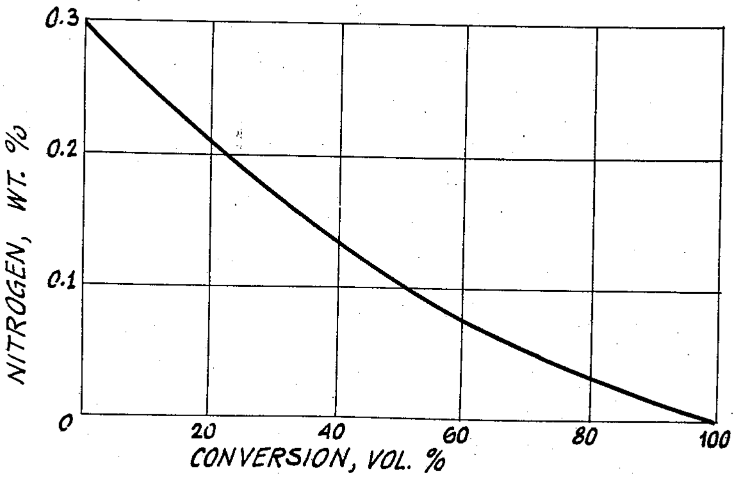


Fig. 3



INVENTORS
Frank G. Ciapetta
William E. Garwood
Harry L. Coonradt
BY
Hastings S. Trigg
ATTORNEY

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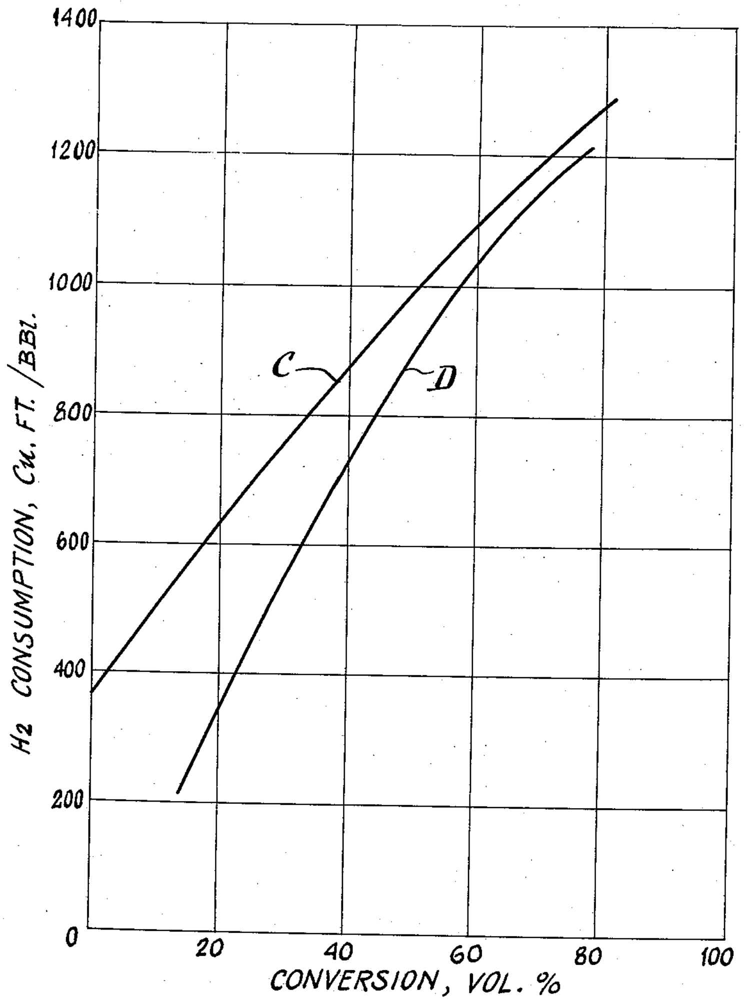
Filed March 9, 1956 2 Sheets-Sheet 2

Fig. 4



INVENTORS
Frank G. Ciapetta
William E. Garwood
Harry L. Coonradt
BY
Hastings S. Trigg
ATTORNEY

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CONTROLLED HYDROCRACKING PROCESS

Frank G. Ciapetta, Upper Darby, Pa., and Harry L. Coonradt, Woodbury, and William E. Garwood, Haddonfield, N.J., assignors to Socony Mobil Oil Company, Inc., a corporation of New York

Filed Mar. 9, 1956, Ser. No. 570,440
3 Claims. (Cl. 208—110)

This invention relates to the catalytic cracking of hydrocarbon fractions. It is more particularly concerned with a controlled process wherein relatively high boiling hydrocarbon fractions are converted into gasoline and fuel oil in the presence of catalysts containing metals of the platinum and palladium series.

In copending application Serial Number 351,151, filed April 27, 1953, now abandoned, and application Serial Number 418,166, filed March 23, 1954, a continuation-in-part thereof, now abandoned, and in copending application Serial Number 825,016, filed July 6, 1959, now U.S. Patent No. 2,945,806, issued July 19, 1960, a continuation-in-part thereof, there is disclosed a process for cracking hydrocarbons in the presence of catalysts comprising metals of the platinum and palladium series deposited upon refractory acidic oxides. It is a preferred feature of that process that the nitrogen content of the charge must be below about 0.1 percent, by weight, and preferably lower than about 0.08 percent, by weight. Under such conditions, by correlation of the temperature and of the liquid hourly space velocity the process could be operated to produce gasoline and/or fuel oil in any ratio varying from substantially 100 percent yield of gasoline to substantially 100 percent yield of fuel oil. In such an operation the cetane index of the fuel oil produced is relatively high and varies dependent upon the degree of conversion in the process.

As is well known to those skilled in the art, however, it is desirable in practical refinery operation to maintain the cetane index of the fuel oil substantially constant regardless of the ratio between the amount of fuel oil produced and the amount of gasoline that may be produced. Thus, depending upon seasonal demands, it will be necessary to produce greater or lesser amounts of gasoline; yet, at the same time it is desirable to maintain the quality of the fuel oil substantially constant. As is also well known to those familiar with the art, greater amounts of hydrogen are consumed in a cracking process to produce fuel oils having relatively high cetane indices. Practically speaking, however, relatively high cetane index fuel oil is not always desired, in order to maintain a competitive quality fuel oil. In such cases, it will be readily appreciated that great savings in operational cost can be effected if the cracking process can be operated under conditions to provide a fuel oil in any yield that has a relatively lower cetane index, but substantially uniform quality.

It has now been found that a process for the cracking of heavy hydrocarbons in contact with hydrogen and with catalysts containing metals of the platinum and palladium series can be operated under conditions whereby there is effected the production of fuel oils having substantially the same cetane index regardless of the yield, which fuel oils have relatively lower cetane index. It has been discovered that such a process can be controlled by operating at substantially constant temperature and by controlling the amount of conversion in the process by regulating the nitrogen content of the hydrocarbon charge stock.

Accordingly, it is an object of this invention to provide an improved process for cracking in the presence of hydrogen and of catalyst comprising platinum or palladium series metals supported upon refractory acidic oxide carriers. Another object is to provide a process for controlling the cetane index in the fuel oils obtained in the cracking process. A further object is to provide a method for regulating the amount of hydrogen consumed in a cracking process carried out in the presence of hydrogen. A further object is to provide a method for producing fuel oils having substantially uniform quality regardless of the yield thereof. A specific object is to provide a method for maintaining the uniformity and quality of fuel oil produced by cracking a relatively high boiling hydrocarbon fraction in the presence of platinum and palladium series metal containing catalysts that involves operating the process at substantially uniform temperature and controlling the amount of conversion in the process by regulating the nitrogen content of the charge.

Other objects and advantages of the present invention can become apparent to those skilled in the art from the following detailed description considered in conjunction with the drawings, wherein:

FIGURE 1 presents the graphic relationship between the volume percent conversion into products boiling at temperatures lower than about 390° F. and the temperature obtained by cracking a typical gas oil in the presence of hydrogen and of a platinum-containing catalyst;

FIG. 2 presents the graphic relationship between the yield of fuel oil and the cetane index thereof, obtained by cracking a typical gas oil in the presence of hydrogen and of a platinum-containing catalyst, both with and without the addition of a nitrogenous compound to the feed;

FIG. 3 presents the graphic relationship between the volume percent conversion into products boiling at temperatures lower than about 390° F. and the weight percent nitrogen in the charge stock obtained by cracking a typical gas oil in the presence of hydrogen and of a platinum-containing catalyst with varying amounts of nitrogen in the charge; and

FIG. 4 presents the graphic relationship between the volume percent conversion into products boiling at temperatures lower than about 390° F. and the hydrogen consumption when a typical gas oil is cracked in the presence of hydrogen and of a platinum-containing catalyst in a process wherein no nitrogen is added to the feed, and also in a process wherein varying amounts of nitrogen are added to the feed.

In general, the present invention provides, in a process for converting a hydrocarbon fraction having an initial boiling point of at least about 400° F., a 50 percent point of at least about 500° F. and an end boiling point of at least about 600° F. and boiling substantially continuously between said initial boiling point and said end boiling point into gasoline and/or fuel oil that comprises contacting said hydrocarbon fraction with a catalyst comprising between about 0.05 percent and about 20 percent by weight of the catalyst of at least one metal of the platinum and palladium series deposited upon a synthetic composite of oxides of at least two metals of groups IIA, IIIB and IV of the periodic arrangement of elements having an activity index of at least 25 in the presence of hydrogen in amounts expressed in molar ratio of hydrogen to hydrocarbon charge varying between about 2 and about 80, at pressures varying between about 100 p.s.i.g. and about 2500 p.s.i.g., at a liquid hourly space velocity varying between about 0.1 and about 10, and at temperatures varying between about 600° F. and about 900° F., the method of operation that comprises operating said process at substantially constant temperature and controlling the amount of conversion into products boiling at temperatures lower than about 390° F. by regulating the nitrogen content of said hydrocarbon fraction within the range varying between about 0.01 percent, by weight, and about 1.0 percent, by weight.

Throughout the specification and the claims, the term "conversion" is intended to be a generic term for the amount of products boiling at temperatures lower than about 390° F. (100-recycle), of gasoline, or of fuel oil obtained in the process. It is expressed in terms of the volume percent of the initial charge which is transformed in the process. The amount of product boiling at temperatures lower than about 390° F. is obtained by subtracting the volume percent of cycle stock (fuel oil) from 100 percent, i.e., from the initial volume of the charge. The expression "(100-recycle)" is an abbreviation for 100 percent minus the volume percent recycle. As the cycle stock (i.e., the effluent boiling at temperatures higher than about 390° F.) is an excellent fuel oil, conversion into fuel oil is the volume percent of product which boils at temperatures higher than about 390° F. The volume percent of conversion into products boiling at temperatures lower than about 390° F. (100-recycle) and the volume percent of conversion into fuel oil totals to 100 volume percent, based upon the initial charge. "Dry gas" refers to the methane, ethane, propane, and ethylene and propylene produced in a cracking process, expressed in terms of weight percent of the initial charge. "Light naphtha" is the product that boils between about 125° F. and about 170° F. The "heavy naphtha" is the product that boils between about 170° F. and about 390° F. The "cetane index" is a measure of ignition quality of a fuel, as described in ASTM test D975-53T, appendix II. The cracking activity of a carrier is expressed in terms of the percent, by volume, of a standard hydrocarbon charge which is cracked, under specific operating conditions, in the "Cat. A" test. This test is described by Alexander and Shimp in National Petroleum News, 36, page R-537 (August 2, 1944). The unit for rating the cracking activity of a material is called the "activity index" (A.I.).

The catalysts utilizable herein are those described in copending application Serial Number 351,151, filed on April 27, 1953, now abandoned; and in the continuation-in-part thereof Serial Number 418,166, filed on March 23, 1954, now abandoned; and in continuation-in-part thereof, Patent No. 2,945,806, filed on July 6, 1959. Briefly, these catalysts comprise between about 0.05 percent, by weight, and about 20 percent, by weight of the final catalyst, preferably between about 0.1 percent and about 5 percent, by weight, of the metals of the platinum and palladium series, i.e., those having atomic numbers of 44–46, inclusive, 76–78, inclusive, supported upon synthetic composites of two or more refractory oxides. The carrier is a synthetic composite of two or more oxides of the metals of groups IIA, IIIB and IVA and B of the periodic arrangement of elements [J. Chem. Ed., 16, 409 (1939)]. These synthetic composites of refractory oxides must have an activity index of at least about 25. They can also contain halogens and other materials which are known in the art as promoters for cracking catalysts, or small amounts of alkali metals that are added for the purpose of controlling the activity index of the carrier. Non-limiting examples of the composites contemplated herein include silica-alumina, silica-zirconia, silica-alumina-zirconia, alumina-boria, silica-alumina-fluorine, and the like. The preferred support is a synthetic composite of silica and alumina containing between about 1 percent, by weight, and about 90 percent, by weight, of alumina. These synthetic composites of two or more refractory oxides can be made by any of the usual methods known to those skilled in the art of catalyst manufacture. Examples of methods of preparing them are set forth in abandoned applications Serial Nos. 351,151 and 418,166 and Patent No. 2,945,806.

The following example illustrates a method of preparing a platinum-containing catalyst utilizable in the process of this invention:

EXAMPLE 1

A synthetic silica-alumina carrier or support containing 10 percent by weight alumina was prepared by mixing an aqueous solution of sodium silicate (containing 158 g. per liter of silica) with an equal amount of an aqueous acid solution of aluminum sulfate containing 39.4 g. $Al_2(SO_4)_3$ and 28.6 g. concentrated H_2SO_4 per liter. This mixture of solutions was dropped through a column of oil, wherein gelation of the hydrogel was effected in bead form. The bead hydrogel was soaked in hot water (about 120° F.) for about 3 hours. The sodium in the hydrogel was then removed by exchanging the gel with an aqueous solution of aluminum sulfate [1.5% $Al_2(SO_4)_3$ by weight] containing a small amount (0.2 percent by weight) of ammonium sulfate. The thus-exchanged hydrogel bead was water-washed. Then, it was dried in superheated steam (about 280–340° F.) for about 3 hours and, finally, calcined at 1300° F. under a low partial pressure of steam for about 10 hours.

The silica-alumina beads were then crushed to pass through a 14-mesh screen and the material retained on a 25-mesh screen (U.S. Standard Screen Series) was used for catalyst preparation. Portions of the crushed, calcined carrier were then barely covered with aqueous solutions of chloroplatinic acid, of concentrations sufficient to produce the desired amount of metal in the finished catalyst. The excess solution was removed by centrifuging. The thus-impregnated carrier was then aged in a lightly covered vessel at 230° F. for 24 hours. The catalyst was treated with hydrogen for 2 hours at 450° F. Then, it was activated in hydrogen for 2 hours at 900° F. before it was used. The catalyst thus prepared contained 0.47 percent platinum, by weight of the catalyst, and the silica-alumina carrier had an activity index of 46.

The charge stocks utilizable herein are hydrocarbon fractions having an initial boiling point of at least about 400° F., a 50 percent-point of at least about 500° F. and an end-boiling point of at least about 600° F. and boiling substantially continuously between said initial boiling point and said end-boiling point. Such charge stocks include gas oils, residual stocks, refractory cycle stocks from conventional cracking, "whole topped crudes," and heavy hydrocarbon fractions derived by the destructive hydrogenation of coal, tars, pitches, asphalts, etc., such as, for example, "middle oil."

As is well known to those skilled in the art, the distillation of higher-boiling petroleum fractions (those boiling at temperatures higher than about 750° F.) must be carried out under vacuum, in order to avoid thermal cracking. Throughout the specification and in the claims, however, the boiling temperatures are expressed in terms of the boiling point at atmospheric pressure. In other words, in all instances, the boiling points of fractions distilled under vacuum have been corrected to the boiling points at atmospheric pressure.

As is well known to those familiar with the art, the term "gas oil" is a broad, general term that covers a variety of stocks. Throughout the specification and in the claims, the term, unless further modified, includes any fraction distilled from petroleum which has an initial boiling point of at least about 400° F., a 50 percent-point of at least about 500° F., and an end-boiling point of at least about 600° F., and boiling substantially continuously between the initial boiling point and the end-boiling point. The portion which is not distilled is considered residual stock. The exact boiling range of a gas oil, therefore, will be determined by the initial distillation temperature (initial boiling point) the 50 percent-point, and by the temperature at which distillation is cut off (end-boiling point).

In practice, petroleum distillations have been made under vacuum up to temperatures as high as 1100–1200° F. (corrected to atmospheric pressure). Accordingly, in the broad sense, a gas oil is a petroleum fraction which boils substantially continuously between two temperatures that establish a range falling within from about 400° F. to about 1100–1200° F., the 50 percent-point being at least about 500° F. Thus, a gas oil could boil over the entire range 400–1200° F. or it could boil over a narrower range, e.g., 500–900° F.

The gas oils can be further roughly subdivided by overlapping boiling ranges. Thus, a light gas oil boils between about 400° F. and about 600–650° F. A medium gas oil distills between about 600–650° F. and about 700–750° F. A heavy gas oil will boil between about 600–650° F. and about 800–900° F. A gas oil boiling between about 800–850° F. and about 1100–1200° F. is sometimes designated as a vacuum gas oil. It must be understood, however, that a gas oil can overlap the foregoing ranges. It can even span several ranges, i.e., include, for example, light and medium gas oils.

As mentioned hereinbefore, a residual stock is any fraction which is not distilled. Therefore, any fraction, regardless of its initial boiling point, which includes all the heavy bottoms, such as tars, asphalts, etc., is a residual fraction. Accordingly, a residual stock can be the portion of the crude remaining undistilled at 1100–1200° F., or it can be made up of a gas oil fraction plus the portion undistilled at 1100–1200° F. A "whole topped crude," as the name implies, is the entire portion of the crude remaining after the light ends (the portion boiling up to about 400° F.) have been removed by distillation. Therefore, such a fraction includes the entire gas oil fraction (400° F. to 1100–1200° F.) and the undistilled portion of the crude petroleum boiling above 1100–1200° F. If it is desired, the residual fractions and the whole topped crude can be deasphalted by any means known to the art. Such treatment, however, is not necessary for charge stocks intended for use in the process of this invention.

The refractory cycle stocks are cuts of conventionally cracked stocks which boil above the gasoline boiling range, usually, between about 400° F. and about 850° F. The refractory cycle stocks can be charged to the process of this invention in conjunction with a fresh petroleum charge stock, or they can be charged alone to the process. The process of this invention is particularly adaptable to the cracking of sulfur-containing charge stocks. The catalysts utilizable in the process of this invention, quite unexpectedly, are not deactivated by sulfur compounds, under the conditions of the process.

The hydrogen pressure used varies between about 100 pounds per square inch gauge and about 2500 pounds per square inch gauge, preferably, however, between about 350 and about 2000 pounds per square inch gauge. The liquid hourly space velocity, i.e., the liquid volume of hydrocarbon per hour per volume of catalyst varies between about 0.1 and 10, preferably, between about 0.1 and 4. Generally, the molar ratio of hydrogen to hydrocarbon charge varies between about 2 and about 80, preferably, between about 5 and about 50.

As has been mentioned hereinbefore, the amount of conversion of a hydrocarbon charge stock into products boiling below about 390° F. can be regulated by varying the temperature. In such an operation, however, the quality of the fuel oil produced, measured in terms of the cetane index will vary with the yield. This will become apparent from the following example.

EXAMPLE 2

The charge stock used in this example was obtained by coking a Mid-Continent residual fraction. This coker gas oil had the following properties:

A.P.I. gravity		33.3
ASTM distillation:		
I.B.P.	° F.	420
50%	° F.	535
E.P.	° F.	664
Sulfur, weight percent		0.48
Nitrogen, weight percent		0.08
Cetane index		47.7

Portions of this coker gas oil were cracked in the presence of hydrogen and of the platinum catalyst described in Example 1 after the latter had reached equilibrium, i.e., had been in continuous operation for more than 5 days. Each run was carried out at a different temperature, using a hydrogen-to-oil molar ratio of 40, a pressure of about 1000 p.s.i.g. and a liquid hourly space velocity of 0.5. The pertinent results of these runs are set forth in Table I.

Table I

Temperature, ° F.	750	770	795
Conversion, volume percent [1]	25.8	43.2	66.5
Dry gas, weight percent	1.5	2.5	4.2
Butanes, volume percent	2.6	6.5	11.8
C_5+ light naphtha, volume percent	4.1	9.6	19.8
Heavy naphtha, volume percent	24.8	35.5	46.6
Fuel oil, volume percent	74.2	56.8	33.5
Cetane index of fuel oil	54.6	53.3	50.5
Hydrogen consumption, c.f./b.	710	895	1,160

[1] Conversion into products boiling at temperatures lower than about 390° F.

The curve in FIG. 1 is based upon the data set forth in Table I. This curve shows the relationship between the volume percent conversion into products boiling at temperatures lower than about 390° F. and the temperature, when a typical gas oil is cracked in the presence of the platinum-containing catalyst. It will be noted that the amount of conversion is a direct function of the temperature, other variables being constant. This, of course, represents one method of controlling the output of the cracking process. The curve in FIG. 1, however, must be considered in conjunction with curve A in FIG. 2. The latter curve, also based upon data set forth in Table I, shows the relationship between the volume percent conversion into fuel oil and the cetane index of the fuel oil. It is to be noted that as the yield of fuel oil varies, the cetane index varies. Such operation does not permit the maintenance of uniform fuel oil quality together with the flexibility in controlling the relative amounts of fuel oil and of gasoline that are produced.

The cracking operation, however, can be operated to produce varying amounts of fuel oil while maintaining substantially uniform quality thereof. This is done by operating at constant temperature and regulating the nitrogen content of the charge to control the amount of conversion. This will be apparent from the following examples.

EXAMPLE 3

The charge stock used in this example was a gas oil obtained by coking a coastal residual which gas oil had been subjected to a hydro-finishing operation to reduce its nitrogen content to 0.04 weight percent. This material had the following properties:

A.P.I gravity		32.6
ASTM distillation:		
I.B.P.	° F.	290
50%	° F.	520
E.P.	° F.	646
Sulfur, weight percent		0.001
Nitrogen, weight percent		0.04

This gas oil was subjected to cracking in the presence of hydrogen and of the equilibrium catalyst described in Example 1. The operation was carried out at a pressure of 1000 p.s.i.g. using a hydrogen-to-oil molar ratio of 40 and a liquid hourly space velocity of 0.5. The catalyst temperature was 760° F. Under these conditions there was effected 76 volume percent conversion into products boiling at temperature lower than about 390° F. Pertinent results are set forth in Table II.

EXAMPLE 4

The charge stock used in this example was another portion of the coastal coker gas oil that had been subjected to hydro-finishing operation to reduce the nitrogen content thereof to 0.1 weight percent. This material had the following properties:

A.P.I. gravity		31.7
ASTM distillation:		
I.B.P.	° F.	276
50%	° F.	520
E.P.	° F.	644
Sulfur, weight percent		0.02
Nitrogen, weight percent		0.10

This gas oil was subjected to cracking in the presence of hydrogen and had the same catalyst used in Example 3. The operation was carried out under the same conditions used in Example 3. Under these conditions, there was effected 51 volume percent conversion into products boiling at temperatures lower than about 390° F. Pertinent data are set forth in Table II.

EXAMPLE 5

The charge stock used in this run is another portion of the coastal coker gas oil that had been subjected to hydro-finishing operation to lower the nitrogen content to 0.12. This material had the following properties:

A.P.I. gravity	31.5.
ASTM distillation:	
I.B.P.	346 ° F.
50%	524 ° F.
E.P.	644 ° F.
Sulfur, weight percent	Less than 0.001.
Nitrogen, weight percent	0.12.

This gas oil was subjected to cracking in the presence of hydrogen and of the catalyst used in Example 3. The conditions of operation were identical with those used in Example 3. Under these conditions there was effected 37 volume percent conversion into products boiling lower than about 390° F. Pertinent data are set forth in Table II.

EXAMPLE 6

The charge stock used in this run was still another portion of the coastal coker gas oil that had been subjected to a hydro-finishing operation to reduce the nitrogen content thereof to 0.24 weight percent. It had the following properties:

A.P.I. gravity		30.7
ASTM distillation:		
I.B.P.	° F.	354
50%	° F.	528
E.P.	° F.	642
Sulfur, weight percent		0.055
Nitrogen, weight percent		0.24

This gas oil was subjected to cracking in the presence of hydrogen and of the platinum catalyst used in the run described in Example 3. The run was operated under the same conditions set forth in Example 3. Under these conditions there was effected 14 volume percent conversion into products boiling lower than about 390° F. Pertinent data are set forth in Table II.

Table II

Example	3	4	5	6
Percent nitrogen in charge	0.04	0.10	0.12	0.24
Temperature, ° F	760	760	760	760
Conversion, volume percent [1]	76	51	37	14
Dry gas, weight percent	2.8	1.9	1.9	0.7
Butanes, volume percent	11.2	8.7	4.7	1.7
C_5+ light naphtha, volume percent	17.9	10.6	6.9	2.0
Heavy naphtha, volume percent	60	43	33	15
Fuel oil, volume percent	24	49	63	86
Cetane index of fuel oil	45	45	44	43.5
Hydrogen consumption, c.f./b	1,200	940	660	220

[1] Conversion into products boiling at temperatures lower than about 390° F.

The curve set forth in FIG. 3 is based upon the data in Table II. This curve presents the graphic relationship between the volume percent conversion into products boiling at temperatures lower than about 390° F. and the nitrogen content of the charge, when a hydrocarbon charge is cracked using the same catalyst temperature but varying the nitrogen content. It will be noted that as the nitrogen content of the charge is varied between about 0 weight percent and about 0.3 weight percent, the charge stock can be cracked at virtually any conversion level while operating at the same temperature throughout. In other words, as compared with the data presented in FIG. 1, the control of the cracking level was achieved by controlling the nitrogen content of the charge, instead of by varying the reaction temperature.

This control of the nitrogen content generally can be effected in several ways or by a combination thereof. One method involves the addition of nitrogenous compounds to the charge stock in amounts sufficient to achieve the desired total nitrogen content that will effect the desired degree of conversion at the operating temperature selected. In general, any nitrogen compound that is capable of being converted into ammonia at the reaction conditions used is applicable. Accordingly, the added compounds can be inorganic nitrogen compounds or they can be organic nitrogen compounds, such as amines, cyclic nitrogen materials, hydrazines and the like. Non-limiting examples of the nitrogen containing compounds utilizable herein are ammonia, 2-methylpyridine, 2-methylpiperidine, pyrrole, pyrrolidine, quinoline, acridine, and carbazole. Another source of added nitrogen is a gas oil, or other hydrocarbon fraction, that has a high nitrogen content, e.g., a California thermally cracked gas oil. It will be appreciated that the regulation of nitrogen content by means of added nitrogen compounds is more generally applicable to charge stocks that have a relatively low nitrogen content. In such a case, the amount of nitrogen compound added will be sufficient to bring the total nitrogen content up to the desired level.

Another method of controlling the nitrogen content, more generally applicable in the case of charge stocks having large amounts of nitrogen, is by means of controlled reduction of the total nitrogen content of the charge. This reduction of nitrogen content can be effected by any of the several means well known to those skilled in the art. A particularly effective method is non-destructive hydrogenation to a degree just sufficient to effect the desired amount of nitrogen removal without materially affecting the other properties of the charge stock. A still further method of regulating the amount of nitrogen in the feed stock is by controlling the ammonia content of the hydrogen-containing recycle gas.

Regardless of the method used for controlling the nitrogen content, the amount of nitrogen compound ultimately in the charge stock will ordinarily vary between about 0.01 weight percent and about 1.0 weight percent, preferably between about 0.01 weight percent and about 0.5 weight percent. In operating the process of this invention wherein the cracking temperature is maintained constant throughout and the amount of cracking is controlled by means of varying the nitrogen content of the feed, the major factor that will effect the desired nitrogen content for any given degree of conversion, is the temperature at which cracking is carried out. The curve in FIG. 3 represents the relationship between the nitrogen content and conversion when operating at a temperature of 760° F. throughout. It will be recognized, of course, that at other operating temperatures a different range of nitrogen content will be used. This range, however, can be expressed by curves that generally parallel the curve set forth in FIG. 3. It is believed to be within the skill of those skilled in the art to determine such relationships between nitrogen content and conversion for any other temperature, using the procedure illustrated hereinbefore.

As will be appreciated, the cracking temperature selected will depend upon the catalyst activity, i.e., the temperature at which a catalyst effects a given amount of conversion. The less active catalysts require higher temperatures. The catalysts also lose activity during use because of the build-up of carbonaceous deposits (coke), or prolonged use, or both. Thus, another advantage of the process of this invention is that the cetane index or the hydrogen consumption, or both can be maintained essentially constant even though the catalyst activity changes. This can be done by raising the temperature. It is more feasible and preferable, however, to accomplish the desired maintenance of uniformity by lowering the amount of nitrogen added to the charge.

As was mentioned hereinbefore, the process for the present invention is particularly applicable in refinery processes in which the cetane index does not have to be relatively high but in which it is highly desirable that fuel oil quality expressed in terms of cetane index should remain substantially constant regardless of the conversion level. That this is achieved in the present process will be apparent from curve B in FIG. 2. This curve based upon the data set forth in Table II represents the relationship between the volume per cent conversion into fuel oil and the cetane index of the fuel oil. As will be apparent from curve B, the cetane index of the fuel oil remains substantially constant regardless of the conversion level. On the other hand, when cracking is carried out by means of controlling the conversion level by means of the temperature (curve A), the cetane index varies considerably with the conversion level. In general, also the cetane index is relatively higher than that expressed by curve B. Yet, a cetane index of such magnitude may not be generally desirable. Indeed, in cases where product uniformity is more desirable, the operation illustrated by curve B is much more desirable on a commercial basis.

A major factor, from an economical standpoint, that effects the choice of a process of the present type is the amount of hydrogen consumption. This is illustrated by the curves in FIG. 4. Curve C represents the graphic relationship between the volume percent conversion into products boiling at temperatures lower than about 390° F. and the amount of hydrogen consumed when the gas oil is cracked in the presence of hydrogen and of the platinum catalyst and by controlling the degree of conversion by varying the temperature. Curve D presents a similar relationship in the case in which the gas oil charge is cracked at a constant temperature, varying the amount of conversion by controlling the nitrogen content of the charge, in accordance with the process of this invention. Particularly at conversion levels lower than about 50 volume percent, considerably more hydrogen is consumed at any given conversion level when the amount of conversion is controlled by means of the temperature. As indicated hereinbefore, however, in many instances the relatively higher cetane index achieved in such an operation is not necessary or desirable. In such a case the amount of hydrogen consumed represented by curve D will be sufficient to achieve the desired cetane index in the fuel oil. Therefore, the amount of hydrogen consumed represented by the difference between curve D and curve C is an excessive amount. This excess represents an unnecessary additional expense in the process which is not warranted by the increase in cetane index and by the loss of ability to maintain product uniformity. Those skilled in the art will readily appreciate that, by means of the process of this invention, such unnecessary expenditure is eliminated and the maintenance of product uniformity is achieved.

Although the present invention has been described with preferred embodiments, it is to be understood that modifications and variations may be resorted to, without departing from the spirit and scope of this invention, as those skilled in the art will readily understand. Such variations and modifications are considered to be within the purview and scope of the appended claims.

What is claimed is:

1. In a process for the reaction of a hydrocarbon fraction having an initial boiling point of at least 400° F., a 50 percent point of at least 500° F. and an end boiling point of at least 600° F. with hydrogen in the presence of a catalyst which comprises between about 0.05 and 20 percent by weight of at least one metal of the platinum and palladium series deposited upon a composite of solid oxides of at least two elements of groups IIA, IIIB and IV of the periodic arrangement of elements, said composite having an activity index greater than 25, wherein there is at all times a net consumption of hydrogen by said fraction and at least periodically the hydrocarbon fraction is converted at a reaction temperature within the range about 600° F. to about 900° F., to lower boiling products, the improved method of operation which comprises: adding nitrogenous compounds to said fraction to increase its nitrogen content and periodically adjusting the quantity of nitrogenous compounds added to effect at least a part of the control over the extent to which said hydrocarbon fraction is converted to lower boiling products, the nitrogen content of the fraction varying from time to time but at all times being within the range about 0.01 to 1 percent by weight of the fraction, and at any given time an increase in added nitrogenous compounds being used to decrease the extent of conversion of the fraction to lower boiling products and a decrease in added nitrogenous compounds being used to increase the extent of conversion of the fraction to lower boiling products, whereby the hydrogen consumed during conversion to lower boiling products is lower than when the same control over the extent of conversion is effected by variation of reaction temperature alone.

2. The process of claim 1 further limited to maintaining the reaction temperature substantially constant within the range 600 to 900° F. and controlling the extent of conversion solely by regulating the nitrogen content of the hydrocarbon fractions undergoing conversion.

3. The process of claim 1 further limited to continuously separating a hydrogen-containing recycle gas from the products of the reaction and returning said recycle gas to the reaction zone and effecting the adjustment in nitrogen content of the hydrocarbon fraction by adjusting the ammonia content of the recycle gas.

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