July 19, 1960 F. G. CIAPETTA 2,945,806

HYDROCRACKING HYDROCARBONS WITH A PLATINUM GROUP METAL DEPOSITED ON AN ACTIVE CRACKING CATALYST BASE

Filed July 6, 1959 4 Sheets-Sheet 1

FIG. 1

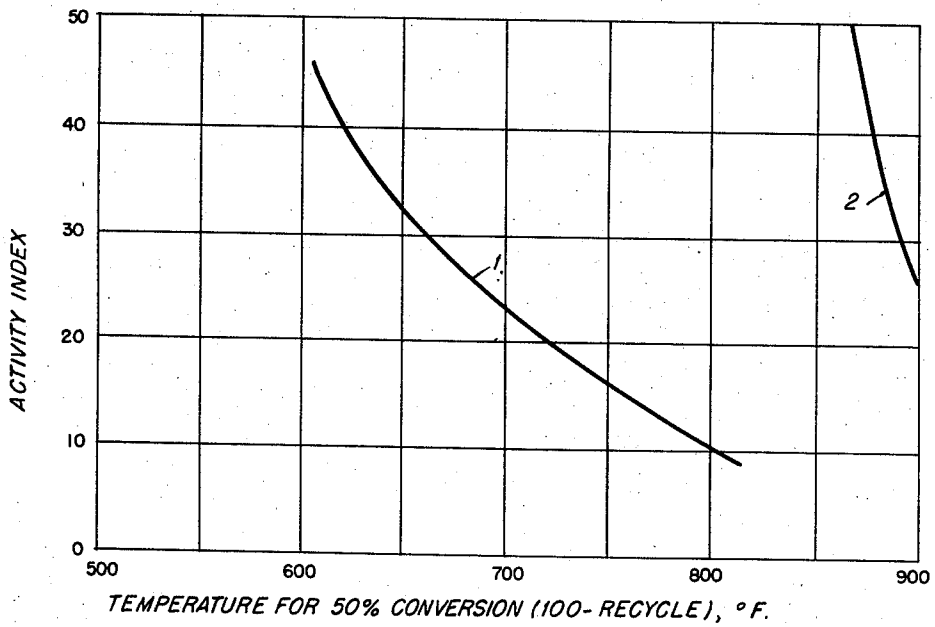
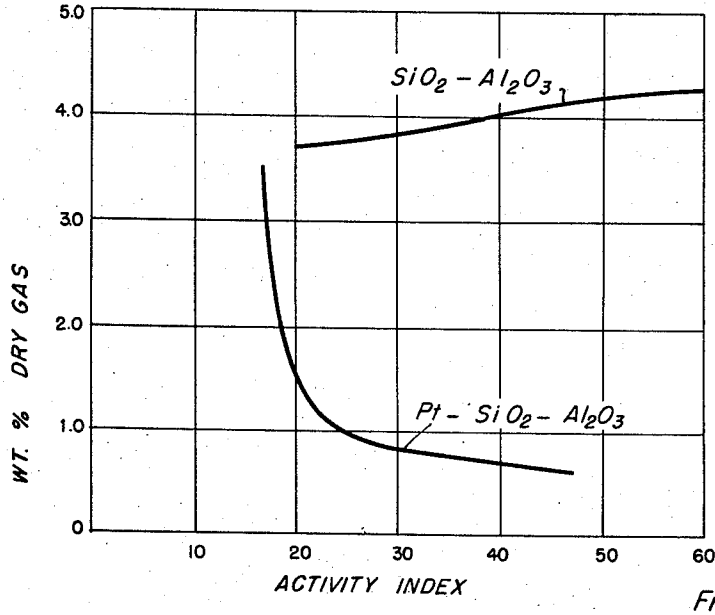


FIG. 2



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FIG. 3

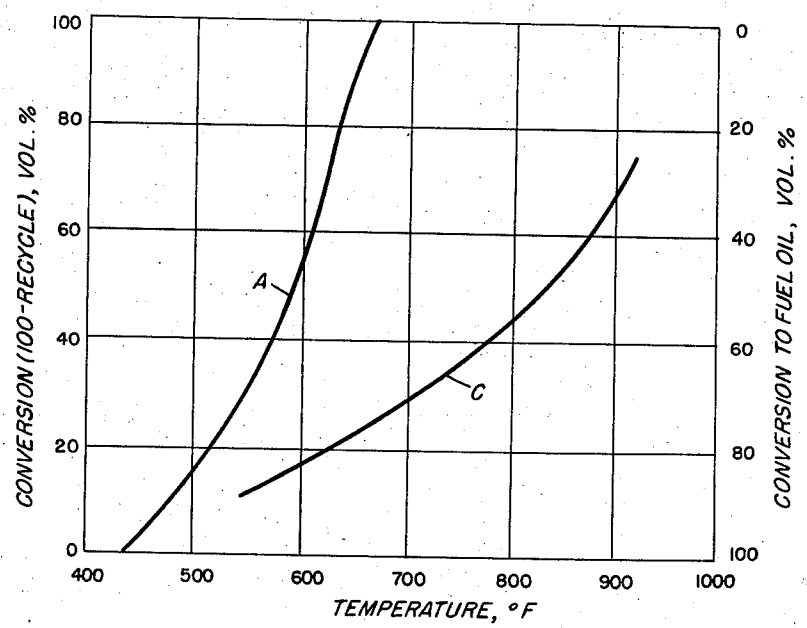
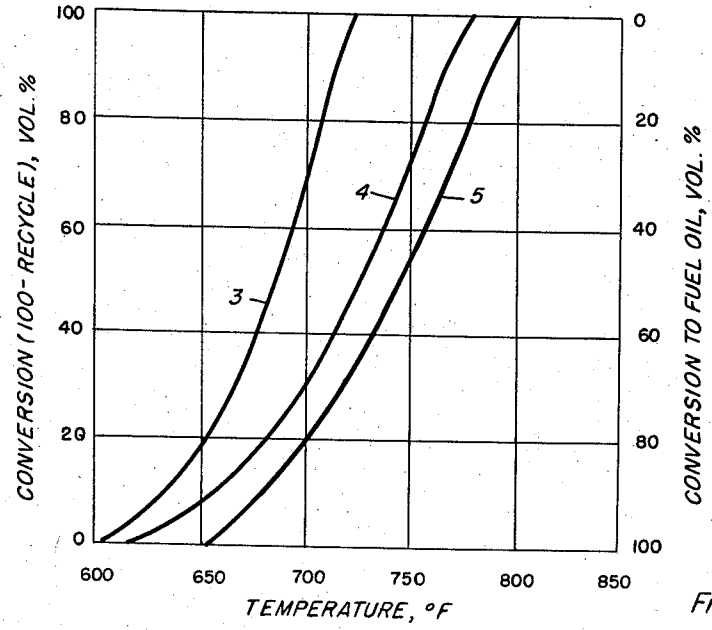


FIG. 4



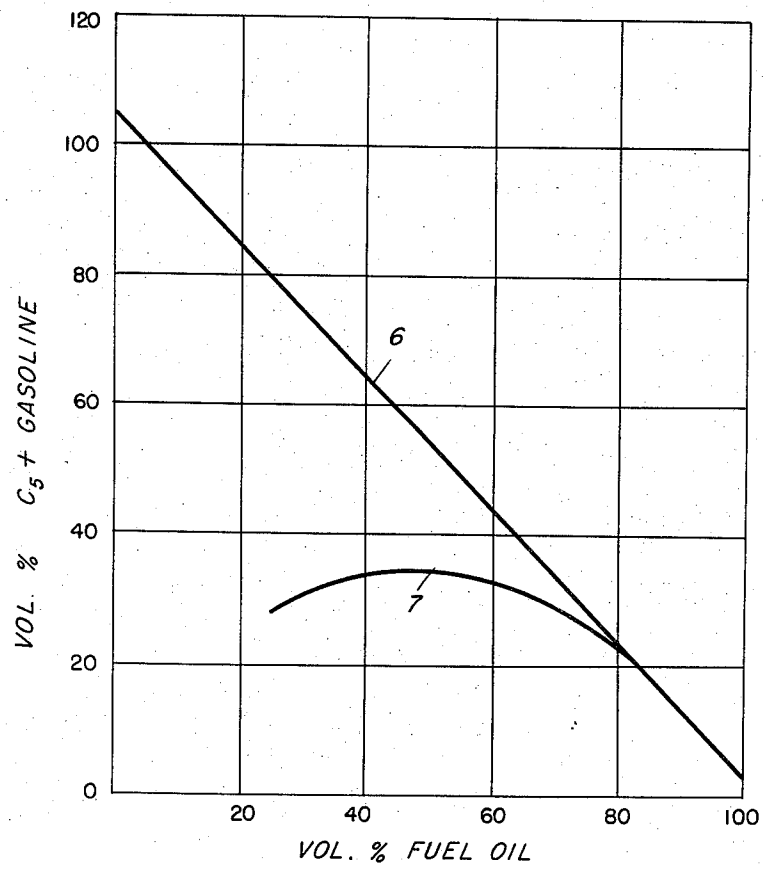
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FIG. 5



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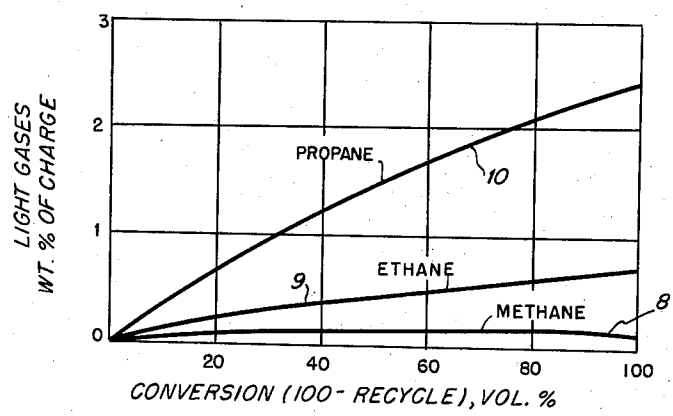


FIG. 6

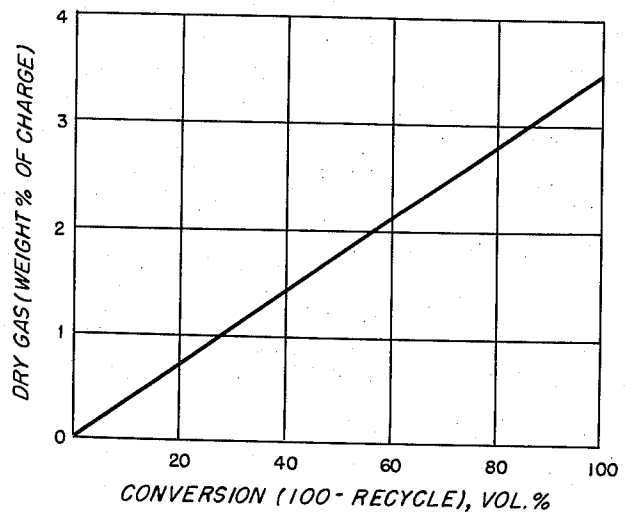


FIG. 7

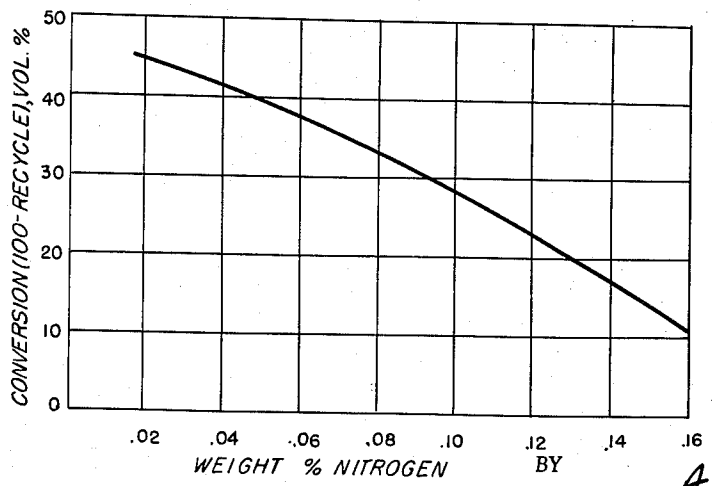


FIG. 8

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HYDROCRACKING HYDROCARBONS WITH A PLATINUM GROUP METAL DEPOSITED ON AN ACTIVE CRACKING CATALYST BASE

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Filed July 6, 1959, Ser. No. 825,016

11 Claims. (Cl. 208—110)

This application is a continuation-in-part of copending application Serial Number 418,166, filed March 23, 1954, now abandoned, which in turn was a continuation-in-part of application Serial Number 351,151, filed April 27, 1953, now abandoned.

This invention relates to the catalytic hydrocracking of hydrocarbons. It is more particularly concerned with a process wherein relatively high boiling hydrocarbon fractions are subjected to cracking in the presence of hydrogen and of supported platinum or palladium catalysts to produce lower boiling, useful hydrocarbon products.

As is well-known to those skilled in the art, cracking is a general term applied to operations wherein mixtures of hydrocarbon molecules having a relatively high molecular weight are converted into mixtures of hydrocarbon molecules having lower molecular weights. If hydrogen is charged to a cracking operation under modified conditions of temperature and pressure, the process is known as hydrocracking. The catalytic cracking of petroleum stocks has been carried out at temperatures of the order of 800–1100° F. The disadvantages of conventional catalytic cracking are, however, the production of relatively large amounts of coke and of dry gas (methane, ethane, ethylene, propylene and propane) and of excess butanes and butylenes. The production of coke and of dry gas constitutes a loss in yield. Indeed, the production of large amounts of dry gas and of excess butanes and butylenes has required the employment of large gas plants to separate propane, propylene, butanes and butylenes (for L.P.G.) from the lighter gases. The large quantity of coke produced in conventional catalytic cracking requires, of course, that the catalyst be regenerated very frequently. In present day operations some of this catalyst is at all times undergoing regeneration.

On the other hand, the hydrocracking catalysts of the prior art can be used for reasonably long periods of time without appreciable loss in activity. Most such catalysts, however, cannot be regenerated.

It is well-known, also, that charge stocks used in the catalytic cracking operations of the prior art have been selected petroleum stocks. Thus, for example, heavy residual stocks have not been suitable for catalytic cracking processes because of their inherent coke-forming characteristics and the excessive amounts of dry gas produced. Consequently, the supply of available cracking stocks has been somewhat restricted.

Even cycle stocks, obtained from the catalytic cracking of non-refractory petroleum cracking stocks, are less desirable as cracking charge stocks in the conventional cracking operations because excessive amounts of dry gas and coke are produced.

When cracking operations are carried out in the presence of hydrogen at relatively high temperatures and under high pressures, i.e., hydrocracking, the aforedescribed limitations on the type of charge stocks are not generally

applicable. Thus, cycle stocks, heavy residuals, etc., can be cracked in hydrocracking operations. Conventional operations of this type, however, have many disadvantages. Thus, in order to maintain catalyst activity at a desired level and to avoid a heavy deposition of coke on the catalyst, it has been found necessary to use inordinately high hydrogen pressures, of the order of at least 3000 pounds per square inch and, preferably, much higher. Such pressures, of course, require the use of expensive, high pressure equipment.

Another undesirable characteristic of the hydrocracking processes of the prior art has to do with sulfur-containing stocks. These stocks have not been charged to hydrocracking operations, unless special catalysts are employed.

Yet, charge stocks otherwise suitable for catalytic cracking operations may contain relatively large amounts of sulfur. The presence of sulfur has made it necessary to use special "sulfur-resistant" catalysts, because many cracking catalysts are rendered ineffective, i.e., "poisoned," by sulfur. In this connection, it must be noted that metallic hydrogenation catalysts cannot be used because of the relative ease with which they become poisoned and, also, because their use results in the formation of large amounts of coke and gas.

Accordingly, it will be appreciated that the provision of a catalytic cracking process involving relatively low temperatures and pressures, which is flexible from the standpoint of the production of useful products, with low production of dry gas and of coke, is highly desirable. Equally desirable is a process for catalytically cracking a wide variety of charge stocks, including the more refractory charge stocks and those containing relatively large amounts of sulfur.

It has now been found that a wide variety of charge stocks, including the more refractory charge stocks and the sulfur-containing charge stocks, can be catalytically cracked, at relatively low temperatures and pressures, to produce high yields of hydrocarbons boiling in the gasoline range, or of distillate fuel oils or both, with a minimum production of dry gas and very limited production of coke. It has now been discovered that the foregoing can be readily effected when the operation is carried out in the presence of hydrogen and of a catalyst comprising platinum or palladium series metals deposited upon a synthetic composite of two or more refractory oxides, which composite has a relatively high cracking activity.

Accordingly, it is an object of this invention to provide an improved catalytic cracking process. Another object is to provide a process for effecting catalytic cracking of hydrocarbon charge stocks to produce gasoline and/or fuel oils in excellent yields. A further object is to provide a process for cracking petroleum cracking charge stocks, with a minimum production of dry gas and of coke. A specific object is to provide a process for hydrocracking hydrocarbon charge stocks, in the presence of hydrogen and of catalysts comprising the metals of the platinum and palladium series deposited upon a synthetic composite of two or more refractory oxides, which composite has a relatively high cracking activity. A further specific object is to provide a process for cracking the refractory charge stocks, such as cycle stocks derived from the conventional catalytic cracking of non-refractory charge stocks. Another specific object is to provide a process for cracking sulfur-containing petroleum charge stocks without poisoning the catalyst with the sulfur. A still further specific object is to provide a process for cracking a wide variety of petroleum charge stocks, at relatively low temperatures and pressures, with a minimum production of dry gas and coke, and with maximum production of liquid prod-

ucts, without poisoning the catalyst. A further object is to provide a process for converting a wide variety of hydrocarbon charge stocks, in a once-through operation, completely into products boiling below about 410° F. with a low production of methane, ethane, and propane and virtually no production of coke. A very specific object is to provide such a process that possesses great flexibility from the standpoint of the amounts and types of products obtained, i.e., the production of gasoline and of distillate fuel oil.

Other objects and advantages of this invention will become apparent to those skilled in the art from the following detailed description considered in conjunction with the figures, wherein

Figure 1 presents a series of curves representing graphically the relationship between the temperature of 50 percent conversion into products boiling below about 410° F. (100-recycle) and the activity index of the catalyst carrier, both with and without platinum thereon, obtained by cracking a typical gas oil;

Figure 2 presents a series of curves showing graphically the relationship between the yield of dry gas and the activity index of the catalyst carrier, both with and without platinum thereon, obtained by cracking a typical gas oil under conditions to yield 50 percent conversion into products boiling below about 410° F.;

Figure 3 presents a series of curves showing graphically the relationship between the temperature and the percent conversion into products boiling below about 410° F. (100-recycle), and the percent conversion into fuel oil, obtained by cracking a typical gas oil in the presence of typical catalysts of this invention and of those of the prior art;

Figure 4 presents a series of curves showing graphically the relationship between the percent conversion into products boiling below about 410° F. (100-recycle) and the percent conversion into fuel oil, and the temperature obtained by cracking a typical gas oil by means of the process of this invention at various space velocities;

Figure 5 presents a series of curves showing graphically the relationship between the volume percent yield of fuel oil and the volume percent yield of C_5+ gasoline, obtained by cracking a typical gas oil by means of the process of this invention and by means of a typical process of the prior art;

Figure 6 presents a series of curves showing graphically the relationship between the percent conversion into products boiling below about 410° F. (100-recycle) and the yield of methane, ethane and propane obtained by cracking a typical gas oil by means of the process of this invention;

Figure 7 presents the graphic relationship between the yield of dry gas and the percent conversion into products boiling below about 410° F. (100-recycle) obtained by cracking a typical gas oil by means of the process of this invention, at various space velocities; and

Figure 8 presents the graphic relationship between the percent conversion into products boiling below about 410° F. (100-recycle) and the nitrogen content of the charge stock, in the cracking process of this invention.

In general, the present invention provides a process for cracking hydrocarbon charge stocks to produce, at least in part, gasoline and/or fuel oil, which comprises contacting 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 with a catalyst that includes 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 two or more refractory oxides, said composite having an activity index of at least 25, in the presence of hydrogen, under a pressure within the range about 100 to 2500 pounds per square inch gauge, at a liquid hourly space velocity within the range 0.1 to about 10 volumes of reactant (measured as 60° F. liquid) per volume of catalyst per hour, at a temperature within the range about 400° F. to 825° F., and using a molar ratio of hydrogen to hydrocarbon charge within the range about 2 to about 80.

As is well-known to those familiar with the art, it has been proposed to increase the octane number of gasolines, naphthas, and kerosenes, by subjecting them to what are termed reforming operations. These involve the use of hydrogen and of catalysts that, in some cases, comprise platinum or palladium on silica-alumina supports. The cracking process of this invention is one which is entirely different and distinct from the reforming processes of the prior art that involve the use of platinum-containing catalysts. The differences are many and real. In the first place, the charge stocks used are not the same. Indeed, the product of the cracking process is the charge for the reforming process. At least a major portion of reforming charge stocks, i.e., gasolines, kerosenes, or naphthas will boil below about 400° F. Usually such charge stocks have initial boiling points of about 60–150° F. Regardless of the initial boiling point, however, the reforming charge stocks have 50 percent points well below 500° F. and end boiling points far below 600° F. The cracking charge stocks contemplated for use in the process of this invention, on the other hand, have initial boiling points of at least about 400° F., 50 percent points of at least about 500° F., and end boiling points of at least about 600° F.

In the second place, the processes are run for two different purposes. Cracking is used to convert significant portions of high boiling hydrocarbon fractions (boiling above about 410° F.) into low boiling hydrocarbon fractions (boiling below about 410° F.). On the other hand, reforming is carried out for the sole purpose of increasing the octane number of low boiling hydrocarbon fractions, with substantially no cracking. Indeed, in reforming processes, an important objective is to minimize cracking.

In the third place, the chemical reactions involved in the two processes are different. In reforming, it is sought to produce gasoline having substantial aromatic hydrocarbon contents from the highly aliphatic reforming charge stocks. Accordingly, reforming involves dehydrogenation, dehydrocyclization, isomerization, etc. Because of these reactions, large amounts of hydrogen are produced during a reforming operation. Cracking, on the other hand, does not necessarily involve these aromatization reactions. The purpose of the cracking process is to convert high boiling, high molecular weight hydrocarbons into lower boiling, lower molecular weight hydrocarbons particularly, in the process of this invention, by selectively rupturing carbon-carbon bonds. As opposed to reforming, this operation consumes hydrogen.

Finally, the cracking process of this invention may be operated at temperatures that are lower than the temperatures at which reforming processes are usually operated. In view of the foregoing discussion, those skilled in the art will appreciate that the reforming processes of the prior art that utilize platinum-containing catalysts, and the cracking process of this invention are entirely different, not in name alone, but in substance and objectives.

Throughout the specification and the claims, the term "C_5+ gasoline" is intended to mean hydrocarbon fractions boiling continuously between temperatures falling within the range varying between about 60° F. and about 410° F. "Conversion," as referred to herein, is a generic term for the amount of products boiling below about 410° F. (100-recycle), obtained in the process of this invention. It is expressed in terms of volume percent of the initial charge which is transformed in the process. The amount of product boiling below about 410° F. is obtained by subtracting the volume percent of material

boiling above 410° F. from 100 percent, i.e., from the initial volume of the charge. The material boiling above 410° F. is commonly termed "recycle" or "cycle stock" herein, and the expression "(100-recycle)" is an abbreviation for 100 percent minus the volume percent recycle. As is discussed hereinafter, the process of this invention may be operated so that all the cycle stock (i.e., effluent boiling above about 410° F.) is excellent fuel oil or it may be operated to produce some material heavier than conventional fuel oil. Conversion to C_5+ gasoline is the volume percent of product boiling between about 60° F. and about 410° F. "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. The cracking activity of a carrier is measured before incorporation of the platinum and palladium series metal and 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 catalytic cracking process of this invention provides many advantages that are not found in the processes of the prior art. These advantages include:

(1) There is real flexibility in the production of gasoline and distillate fuel oil. If desired, this process may be operated to produce, on a once-through basis, only these two components and to produce them in any desired ratio from 100 percent gasoline to 100 percent fuel oil. The fuel oil so produced will meet the terms of the specifications for No. 1 or No. 2 fuel oil set forth in "ASTM Standards on Petroleum Products and Lubricants," November 1952, Specification D396–48T, on page 180. On the other hand, the process may be operated to produce some material heavier than No. 2 fuel oil, which material may be recycled to the process to be further converted or it may be passed on to some other processing unit for further treatment. The conditions of operation may be easily controlled to achieve any of these conversions.

(2) The great flexibility of operation referred to in paragraph (1) is accomplished by relatively small changes in operating conditions. For example, a relatively small change in reaction temperature, other operating conditions remaining constant, greatly alters the ratio of gasoline to higher boiling material in the product.

(3) The distillate fuel oils produced in the process are of very high quality. They are substantially saturated and have excellent diesel indexes and stability characteristics. Furthermore, the fuel oils are not refractory in nature. Therefore, they are excellent charge stocks for other cracking processes.

(4) The amount of dry gas produced is very small and coke is formed in almost negligible quantities. The amount of methane and ethane is almost negligible, and very little propane is produced. Accordingly, the gas plant, if required at all, is very small. On the other hand, the gas plants accompanying the conventional catalytic cracking processes of the prior art are, by comparison, very large. Further, as a result of the small amount of dry gas produced, the recycle hydrogen from the reactor has a high degree of purity.

(5) The process of this invention can be operated to tolerate high contents of sulfur in the charge stock, without poisoning the catalyst. The product is substantially completely desulfurized. Furthermore, the sulfur is removed as hydrogen sulfide.

(6) The catalysts used in the process of this invention remain active over very long periods of time, usually months. In contrast with the catalyst which have been proposed for destructive hydrogenation, the catalysts of this invention can be regenerated in situ, when and if the activity decreases after a period of use. It has been found that regeneration can restore the activity of the catalyst to the initial activity level of the fresh catalyst. Because of these properties, the catalysts can be used for extremely long periods of time, with infrequent regeneration, before replacement is required.

(7) The process of this invention is very selective. As is well-known to those familiar with the art, in the processes of the prior art, splitting of the carbon-carbon bond is random and uncontrolled so that cracking occurs at the end of the hydrocarbon chains, as well as near the center. As a result, large amounts of methane, ethane, etc., are produced. Consequently, large amounts of hydrogen are consumed in the production of undesirable products. The process of this invention, on the other hand, is more selective for "center cracking," i.e., rupture of the hydrocarbon chain near its middle. Both cracked fragments, therefore, have sufficient chain length to produce hydrocarbons useful in gasoline. As a result, the hydrogen consumed in the production of undesirable products is minimized.

(8) The cracking process of this invention may be operated at temperatures and under pressures generally lower than those of the hydrocracking processes of the prior art. Extremely high pressure equipment, therefore, is not required. Consequently, the amount of capital investment is substantially reduced. The advantages, from the standpoint of economics, of operating at lower temperatures will be apparent to those skilled in the art.

The carriers or supports for the catalysts utilizable in the process of this invention are synthetic composites of two or more refractory oxides, which composites are acidic in nature. Generally, this group includes oxides of the metals of groups IIA, IIIB, and IVA and B of the periodic arrangement of elements [J. Chem. Educ., 16, 409 (1939)]. As will be demonstrated hereinafter, however, in order to achieve effective cracking and production of small amounts of dry gas, the activity index of the catalyst carrier must be at least about 25. The synthetic composites of refractory oxides can also contain halogens and other materials which are known in the art as promoters for cracking catalysts. The synthetic composites can also contain small amounts of alkali metals, added for the purpose of controlling the activity index of the carrier. Non-limiting examples of the synthetically produced composites contemplated herein include silica-alumina, silica-zirconia, silica-alumina-zirconia, silica-alumina-thoria, alumina-boria, silica-magnesia, silica-alumina-magnesia, silica-alumina-fluorine, and the like. A preferred support is a synthetic composite of silica and alumina which contains between about one percent, by weight, and about 90 percent, by weight, of alumina.

There appears to be nothing critical about the manner in which the carriers are prepared. They may be made by any of the usual methods well-known to those skilled in catalyst manufacture. As was stated hereinbefore, the silica-alumina carriers are prepared. Thus, the following methods, applied, to preparing silica-alumina composites, can be used as guides to preparing the other composites contemplated herein. The carrier can be prepared by adding an aqueous solution of a strong acid, such as sulfuric, nitric, or hydrochloric acid, to an aqueous solution of sodium silicate to precipitate a silica hydrogel. After the silica hydrogel is washed with water to remove sodium ions, it can be composited with the desired amount of purified alumina hydrogel. The alumina hydrogel can be prepared by adding ammonia or an alkali-metal hydroxide to an aqueous solution of an aluminum salt, e.g., aluminum nitrate, sulfate, or chloride. The carrier can also be prepared by dispersing silica hydrogel in an aqueous solution containing the required amount of a salt of aluminum, and then adding sufficient aqueous ammonia to precipitate the alumina. The support can also be prepared by mixing a

wet alumina hydrogel with a calcined silica to form an intimate mixture of the two components. Another method for preparing the base involves adding an aqueous acidic solution, containing the required amount of aluminum salt, to an aqueous solution of sodium silicate, thus precipitating the silica and the alumina simultaneously. The latter type of operation can be carried out, in accordance with the method disclosed in United States Letters Patent No. 2,384,946, to produce the carrier in a hydrogel bead form. This constitutes a preferred method of preparing the carrier.

In accordance with this preferred method, an aqueous solution of sodium silicate is mixed rapidly with an aqueous sulfuric acid solution containing the required amount of an aluminum salt, the resulting solution falling into a column of oil, wherein gelation occurs to produce hydrogel beads. The formed beads are then exchanged with an aqueous acid solution of an aluminum salt, thus removing the sodium ions and incorporating alumina into the beads. The exchanged beads are then washed with water before drying and calcining.

In all the preparations aforedescribed, the final composites are washed thoroughly with water to remove any alkali-metal ions that may be present. Then the composites are dried at about 220° F. and, finally, calcined in air at 900–1400° F.

A typical method for preparing a halogen-containing carrier involves impregnating the synthetic oxide composite carrier with an aqueous solution of the corresponding ammonium halide, e.g., ammonium chloride or fluoride. The thus impregnated carrier is then dried at about 1000° F. to decompose the ammonium halide with liberation of ammonia.

In some instances, it may be desirable to reduce the activity index of a carrier from some relatively high value, but never, of course, to below 25. This can be accomplished by several methods, all well-known in the art. For example, it can be accomplished by steaming the carrier at temperatures of between 900° F. and about 1400° F., under steam pressures of between atmospheric and about 300 pounds per square inch gauge. Ordinarily, the time of treatment will be between about 50 hours and about 100 hours, although longer or shorter periods can be used. The activity index can be lowered also by treating the carriers at temperatures of between about 1600° F. and about 1800° F., without the use of steam. In still another method, the carrier can be treated with water at 300–800° F. under pressures of 300–3000 pounds per square inch gage, for periods of time varying between about 1 hour and about 100 hours.

The amount of metal of the platinum or palladium series deposited upon the carrier should be within the range about 0.05 percent, by weight, to about 20 percent, by weight, of the final catalyst, preferably between about 0.1 percent and about 5 percent. The metals of the platinum and the palladium series are those having atomic numbers of 44–46, inclusive, and 76–78, inclusive. Platinum and palladium are especially preferred.

The metal deposited upon the carrier can be a single metal of the platinum and palladium series, or it can be a mixture or alloy of two or more such metals. Mixtures and alloys of other metals with metals of these series are also contemplated. The metal can be deposited upon the carrier in any suitable manner. A preferred method is to admix the synthetic oxide composite carrier with an aqueous solution of a halogen-containing acid of the desired metal, for example, chloroplatinic or chloropalladic acid, or of the ammonium salts of these acids, in amounts such that the liquid is substantially completely taken up by the carrier and in a concentration to produce the desired amount of metal in the finished catalyst. The mixture is then dried (usually at temperatures of about 200° F. to 250° F. for about 16 hours) and treated with hydrogen at elevated temperatures (about 400° F. to about 500° F. for about 2–4 hours), to reduce the chloride to the metal and to activate the catalyst.

The following examples are illustrative of methods, all well-known to those familiar with the art, of preparing typical cracking catalysts of the prior art and the platinum- or palladium-containing catalysts utilizable in the process of this invention, and of methods of modifying the properties thereof:

EXAMPLE 1

Catalyst preparation

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 then 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 percent $Al_2(SO_4)_3$ 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 about 14–25 mesh (U.S. Standard Screen Series). Portions of the crushed calcined carrier were then 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. Each of the thus-impregnated carriers was dried at 230° F. for 24 hours. Each catalyst thus obtained was treated with hydrogen for four hours at 400° F. Then, it was activated in hydrogen at 1000° F. for 16 hours before it was used. Catalysts A, B, D and E were prepared in this manner, whereas catalyst C was the aforedescribed carrier containing no platinum or palladium metal.

Catalysts F, G, H, I and J were produced by treating portions of the crushed, calcined silica-alumina gel in a 5-gallon sealed autoclave containing about 1800 cc. of water. Each portion of carrier was treated for one hour at temperatures and pressures sufficient to lower the A.I. to the desired level. These conditions are:

Carrier for Catalyst	Temp., ° F.	Pressure, p.s.i.
F	300	125
G	400	225
H	475	525
I and K	525	900
J	600	1,200

The carriers thus obtained were then dried, calcined, and impregnated with platinum, as aforedescribed, and finally dried and activated in the presence of hydrogen, also as described hereinbefore. Catalyst K was a silica-alumina carrier having a reduced activity index but containing no platinum.

The carrier for catalyst L was prepared by covering a portion of the carrier used for preparing catalysts A, B, D and E with an aqueous solution of ammonium fluoride (8 percent NH_4F), and letting it stand for about 3 hours. The excess solution was then removed by suction filtration. The carrier thus prepared was dried at about 280° F. for about 65 hours, and calcined in air for about 3 hours at 1100° F. The calcined base was then impregnated with platinum, dried, and activated in hydrogen, as aforedescribed.

The alumina-boria carrier of catalyst M was prepared

by covering commercial activated alumina (8–14 mesh) with a hot aqueous solution of boric acid (0.3 g. H_3BO_3 per cc.), maintained at about 200° F., for about one hour. The excess solution was decanted, and the impregnated alumina was dried at about 280° F. for about 16 hours. This impregnation and drying procedure was repeated two more times. (The activated alumina was a commercial material prepared by the dehydration of aluminum trihydrate.) After the third impregnation and drying, the carrier thus obtained was calcined for about 16 hours, at 1000° F. The calcined carrier was crushed to 14–25 mesh (U.S. Standard Screen Series). Then, the carrier was impregnated with platinum and activated, as aforedescribed.

The carrier for catalyst N was prepared from a chlorine-free commercial alumina-silica gel (8–14 mesh, and containing about 5 percent silica by weight), produced by mixing alumina hydrogel with a suitable proportion of silica hydrogel, in amounts to the final desired weight proportion. The commercial alumina-silica gel was impregnated twice with an aqueous solution of hot boric acid (0.22 g. H_3BO_3 per cc.), using the procedure set forth in the description of the preparation of catalyst M. The impregnated alumina thus obtained was dried at about 280° F. for about 16 hours, and calcined in air for about 16 hours, at about 1000° F. The calcined carrier was crushed to 14–25 mesh, impregnated with platinum, and activated as aforedescribed.

The pertinent properties and analyses of these catalysts are set forth in Table I.

TABLE I.—CATALYST COMPOSITION

Catalyst	Metal	Carrier	A.I. of Carrier
A	1.8% Pt	88.4% SiO_2—9.8% Al_2O_3	46
B	0.45% Pt	89.55% SiO_2—10% Al_2O_3	46
C	None	90% SiO_2—10% Al_2O_3	46
D	0.43% Pt	89.61% SiO_2—9.96% Al_2O_3	46
E	0.42% Pt	89.62% SiO_2—9.96% Al_2O_3	46
F	0.48% Pt	89.57% SiO_2—9.95% Al_2O_3	38
G	0.41% Pt	89.63% SiO_2—9.96% Al_2O_3	33
H	0.41% Pt	89.63% SiO_2—9.96% Al_2O_3	29
I	0.58% Pt	89.48% SiO_2—9.94% Al_2O_3	25
J	0.48% Pt	89.57% SiO_2—9.95% Al_2O_3	17
K	None	90% SiO_2—10% Al_2O_3	26
L	0.5 Pt	87.97% SiO_2—9.77% Al_2O_3—1.75% F.	48
M	0.41% Pt	90.4% Al_2O_3—9.6% B_2O_3	45
N	0.64% Pt	84.7% Al_2O_3—5% SiO_2—10.3% B_2O_3.	45

As has been mentioned hereinbefore, an important desideratum of a cracking process is that the amount of dry gas be virtually nil. In order to achieve this with the cracking catalysts utilizable in the process of this invention, it has been found that the activity index of the carrier must be at least about 25. This is demonstrated by the results obtained in the runs described in Example 2.

EXAMPLE 2

To show the effect of activity index

The charge stock used in these runs was a light gas oil. This oil was distilled from an East Texas crude and had the following properties: an A.P.I. gravity of 37.5; an initial boiling point of 416° F.; a 50 percent point of 516° F.; an end point of 622° F.; and a sulfur content of 0.14 percent by weight. This light East Texas gas oil was subjected to cracking under temperature conditions to produce about 50 percent conversion to products boiling below about 410° F. (100-recycle), using catalysts comprising platinum deposited upon silica-alumina carriers having various activity indexes. These catalysts are catalysts E through J, inclusive, as set forth in Table I. Each run was carried out under a hydrogen pressure of 1000 pounds per square inch gauge, using a hydrogen to hydrocarbon ratio of 10, and a liquid hourly space velocity of one. In each run, the temperature for 50 percent conversion into products boiling below about 410° F., the amount of dry gas produced, and the amount of C_5+ gasoline produced were noted. The pertinent data are set forth in Table II.

TABLE II

Catalyst, Wt. percent, Pt		A.I.	Temp., ° F. for 50% Conv.	Product Distribution at 50% Conversion—C_3 and Lighter, Wt. percent	Vol. percent C_5+ Gasoline
E	0.42	46.0	603	0.7	50.5
F	0.48	38.0	623	0.8	51.5
G	0.41	33.0	648	0.8	50.2
H	0.41	29.0	674	0.9	49.8
I	0.58	25.0	703	0.9	53.5
J	0.48	17.0	720	3.4	52.5

Figures 1 and 2 are based on the data set forth in Table II. Referring now to Figure 1, curve 1 demonstrates the relationship between the activity index of the silica-alumina carrier and the temperature required to obtain a 50 percent conversion of the gas oil charged into products boiling below about 410° F. (100-recycle), when the carriers contain platinum. Curve 2 demonstrates a similar relationship for an identical silica-alumina carrier containing no platinum.

It will be noted, in Figure 1, that there is a steady increase in the temperature requirements for a platinum catalyst used in the process of this invention (curve 1) to attain 50 percent conversion of the charge, as the activity index of the carrier decreases. As the activity index approaches about 10, the temperature requirement is about 800° F. On the other hand, it will be noted that the silica-alumina carriers containing no platinum (curve 2) require much higher temperatures regardless of the activity index of the carriers.

There is a further factor, however, which limits the activity index of the carrier for the catalysts utilizable in the process of this invention. This is the amount of dry gas produced in the process. Figure 2 shows the relationship between the activity index of the silica-alumina carrier and weight percent of dry gas produced at a 50 percent conversion to products boiling below about 410° F., for the platinum catalysts contemplated herein and a similar relationship for silica-alumina carriers without platinum. It will be noted that, in the absence of platinum, the yield of dry gas is relatively high and virtually unaffected by the activity index. On the other hand, the amount of dry gas produced when using a platinum-containing catalyst is very low. As the activity index of the silica-alumina carrier of these platinum-containing catalysts approaches about 25, however, there is a sudden, sharp increase in the production of dry gas. Therefore, although conversion can be achieved at about 800° F. with platinum on a silica-alumina carrier having an activity index of about 10, the amounts of dry gas produced are undesirably large. Accordingly, the activity index of the carriers for the cracking catalysts utilizable in the process of this invention is critical and must be maintained higher than at least about 25, ordinarily between about 25 and about 52. Preferably, the activity index of the carrier should be between about 28 and about 52.

After the catalyst has been in service for a substantial period of time, reactivation of the catalyst may be necessary. This is accomplished readily by contacting the catalyst with air or other oxygen-containing gases at elevated temperatures, in order to burn carbonaceous deposits from the catalyst. Generally, regeneration is effected at temperatures of about 700° F. to 950° F., commencing with a gas of low oxygen-content and gradually increasing the oxygen concentration throughout the regeneration period which may last from about 6 hours to about 24 hours. It is important to maintain the regeneration temperature below about 1100° F., as higher temperatures tend to impair the catalyst activity. The regenerated catalyst is then treated with hydrogen at

temperatures of about 900° F. to about 1000° F. for about 2–10 hours to complete reactivation.

Cracking, in accordance with this invention, is carried out at relatively low temperatures. This is illustrated by the data obtained from the runs described in Example 3.

EXAMPLE 3

To show the effect of temperature

The light East Texas gas oil defined in Example 2, was contacted at several temperatures, in once-through operations, in the presence of catalyst A, containing 1.8 percent platinum. The operation was carried out at a liquid hourly space velocity of one, under a hydrogen pressure of 500 pounds per square inch gauge, and using a hydrogen to hydrocarbon molar ratio of 9.5. Typical analyses of the products at the points of 0 percent, 50 percent, 70.8 percent and 100 percent conversions into products boiling below about 410° F. are set forth in Table III.

For the purpose of comparison, the same gas oil was contacted, in once-through operations, at various temperatures in the presence of catalyst C, the silica-alumina composite containing no platinum. This is a typical cracking catalyst of the prior art. One set of runs was carried out in the presence of hydrogen under the same conditions of space velocity, hydrogen to hydrocarbon ratio, and hydrogen pressure used in the runs with catalyst A. Another set of runs was carried out in the absence of hydrogen, using a space velocity of one and about atmospheric pressure, typical conditions of the conventional cracking processes.

The run conditions and the analyses of the products obtained in these runs at 50 percent and at 70.8 percent conversion levels are set forth in Table III.

TABLE III

Catalyst	A	A	A	A	C	C	C	C
Platinum Content, Percent	1.8	1.8	1.8	1.8				
H_2/HC molar ratio	9.5	9.5	9.5	9.5	9.5	9.5	0	0
H_2 pressure, p.s.i.g.	500	500	500	500	500	500	Atm.	Atm.
L.H.S.V.	1	1	1	1	1	1	1	1
Temperature, ° F.	410	585	620	680	835	902	845	902
Conversion, Vol. Percent [1]	0	50.5	70.8	100.0	50.0	70.8	50.0	70.8
C_3 and lighter, Wt.percent	0.2	1.7	2.4	3.4	2.0	8.5	6.2	21.0
Butanes, Vol. percent	0.5	5.2	7.8	11.0	6.0	17.3	13.5	29.0
C_5+ Gasoline, Vol. percent	2.5	53.4	76.0	104.8	37.5	48.9	33.8	30.0
Fuel Oil, Vol. percent	100	50.0	29.2	0	60.0	29.2	50.0	29.2

NOTE.—All volume and weight percent figures are based on the original charge.

[1] Conversion to products boiling below about 410° F. (100-recycle).

Figure 3 is based on the data set forth in Table III, and shows the relationship between the percent conversion to products boiling below about 410° F. (100-recycle) and to fuel oil, and the temperature. The curve designated by the letter "A" shows the relationship between the percent conversion into products boiling below about 410° F. (100-recycle) and into fuel oil, and the temperature, when using freshly prepared catalyst A (1.8 percent platinum deposited on silica-alumina). The curve designated by the letter "C" represents a similar relationship, for an identical, freshly prepared silica-alumina carrier, containing no platinum.

From the curves in Figure 3, it will be noted that with the freshly prepared platinum-silica-alumina catalyst (curve A), high conversions into products boiling below about 410° F. (100-recycle) (over 50 percent) are effected at temperatures of about 600–700° F. Substantial conversions into products boiling below 410° F. are achieved, however, at temperatures as low as about 500° F. Complete conversion into substantially fuel oil occurs at about 400° F. On the other hand, it will be noted that substantially higher temperatures are required to attain similar conversions when using an unplatinized silica-alumina catalyst (curve C). Additionally, the product distribution is poorer, as will be discussed hereinafter.

The range of operating temperatures suitable for use in this invention will vary somewhat with the type of carrier used for the platinum or palladium series metal, with the type of charge stock and with the type and quantity of certain impurities, such as nitrogen compounds, in the charge stock. In addition, the range of operating temperatures of the process of this invention also will vary, depending upon the space velocity employed and upon whether the catalyst is freshly prepared or aged, i.e., "stabilized." This is illustrated by the results of the runs described in Example 4.

EXAMPLE 4

Relationship between temperature and space velocity

The light East Texas gas oil described in Example 2 was subjected to cracking, in the presence of catalyst B (0.45 percent platinum on silica-alumina of 46 A.I.), which had been stabilized by using it continuously in the cracking process of this invention for about four days. Cracking was effected at various temperatures sufficient to achieve 0–100 percent conversion into products boiling below about 410° F. (100-recycle) and to fuel oil. The pressure employed was 1000 pounds per square inch gauge, the hydrogen-to-hydrocarbon molar ratio was 40, and the space velocity was 0.5. The volume percent conversion into products boiling below about 410° F. (100-recycle) and to fuel oil at each operating temperature are set forth in Table IV.

Similar runs, using the same stabilized catalyst, pressure and hydrogen-to-hydrocarbon ratio, were made on the light East Texas gas oil, at space velocities of 1.0 and of 1.5. The pertinent results of these runs are also presented in Table IV.

TABLE IV

Space Velocity	Temp., ° F.	Products Boiling Below About 410° F., Vol. Percent	Fuel Oil Vol. Percent
0.5	610	0	100
0.5	640	13	87
0.5	685	45	55
0.5	700	69	31
0.5	745	100	0
1.0	620	0	100
1.0	680	18	82
1.0	730	55	45
1.0	757	79	21
1.0	780	100	0
1.5	655	0	100
1.5	720	33	67
1.5	758	61	39
1.5	800	100	0

The curves of Figure 4 are based upon the data set forth in Table IV. These curves define the relationship between the volume percent conversion into products boiling below about 410° F. (100-recycle) and into fuel oil, and the temperature, at space velocities of 0.5 (curve 3), 1.0 (curve 4) and 1.5 (curve 5).

A comparison of curve A of Figure 3 with curve 4 of Figure 4 (for runs made at the same space velocities)

shows that the aging or stabilization of the catalyst increases the temperature requirements. Likewise, using the aged catalyst under conditions comparable, except for the space velocity, there is a substantial variation in the temperature requirements.

The operating temperatures for the catalysts used in the process of this invention will fall within the range 400 to 825° F. The precise optimum range within these limits will depend somewhat on the particular carrier used for the platinum or palladium series metals and for a given catalyst it will depend upon the age of the catalyst and the space velocity employed. This can readily be determined, by those skilled in the art, by plotting temperature versus the percent conversion into products boiling below about 410° F. (100-recycle) and into fuel oil, as was done in Figure 3. Preferred operations are carried out at temperatures within the range 400 to 800° F.

Another outstanding feature of the process of this invention will also be apparent from the curves set forth in Figures 3 and 4, and from Table III. This feature is the complete flexibility of the ratio between the production of products boiling below about 410° F. (100-recycle) and of distillate fuel oil that is possible with this process. The product boiling below about 410° F. is substantially all gasoline, as most of the butanes produced are used with the C_5+ gasoline to meet vapor pressure requirements. The material boiling above 410° F. is a good recycle stock. The process also may be operated so that all of this recycle stock is an excellent distillate fuel oil. The recycle stock generally has a high hydrogen-to-carbon ratio and has an end point much lower than the end point of the initial charge stock. It is to be noted from curve A of Figure 3 that, with the charge stock and catalyst used to determine this curve and depending upon the temperature of operation, other conditions being constant, it was possible to produce substantially gasoline and fuel oil in any ratios. Thus, when operating at lower temperatures, substantially all the charge stock was converted into fuel oil. When operating at higher temperatures, on the other hand, substantially all the charge stock was converted into substantially gasoline. When operating at intermediate temperatures, any ratio of fuel oil to substantially gasoline could be achieved. The variation of the ratio of substantially gasoline to distillate fuel oil is very sensitive to temperature. This is apparent from the steep slope of curve A of Figure 3, i.e., a change in the ratio of substantially gasoline to distillate fuel oil can be achieved with relatively slight variation in temperature. In so far as is now known, such flexibility of operation has not been possible with the processes of the prior art.

Referring particularly to Table III, it will be noted also that, at complete production of distillate fuel oil, the small amount of gasoline produced is not from cracking as such, but from hydrogenation. Significantly, the amount of propane and of lighter gases produced at any conversion level is very low. Further, very little, if any, excess butanes are produced at any conversion level, over and above the amount which can be used for blending into finished gasoline. In the process of this invention, therefore, substantially all the charge stock, at any conversion level, in a once-through operation, may be converted into substantially gasoline or into distillate fuel oil, or both. The process may also be used to produce some material heavier than fuel oil where this is desired. Thus, the process achieves efficient conversions, with minimum losses from coke, dry gas and excess butanes, at any conversion level.

The efficiency of the cracking process of this invention will be at once apparent from the curves set forth in Figure 5. In this figure, curve 6 shows graphically the relationship between the volume percent conversion into fuel oil and the volume percent production of C_5+ gasoline, when the light East Texas gas oil is cracked by means of the process of this invention. Curve 7 defines the same relationship when the same gas oil is cracked by means of a conventional cracking process. These curves are based upon the product data set forth in Table III. It will be noted (curve 6) that substantially all of this charge stock is converted, by the present process, into fuel oil and/or gasoline, regardless of the conversion level. On the other hand, such a relationship holds true, in the prior art cracking processes (curve 7), only at conversions into fuel oil of 80–100 volume percent (up to about 20 volume percent conversion into products boiling below about 410° F.). Below 80 volume percent conversion into fuel oil (i.e., above about 20 volume percent conversion into products boiling below about 410° F.) the amount of gasoline produced diminishes, first slowly, and then very rapidly at conversion levels (to products boiling below about 410° F.) greater than about 50 volume percent. That is why the conventional cracking processes cannot be operated feasibly at high once-through conversion levels. It will be appreciated, therefore, that the conventional cracking processes lack the flexibility of once-through operation which can be attained by the process of this invention.

As conventional cracking processes are usually operated at 50 percent conversion into fuel oil, the comparison will now be made at this level. In the present process (curve 6), the amount of C_5+ gasoline produced at this conversion level was 53.4 volume percent. The loss to dry gas was low, and, as stated hereinbefore, the loss to coke was nil. On the other hand, at the 50 percent conversion level in a conventional cracking process (curve 7), only 33.8 volume percent of C_5+ gasoline was produced. The difference in gasoline yield, i.e., the loss, is due to the large amounts of dry gas, excess butanes, and coke. It will be appreciated, therefore, that the process of this invention is much more efficient, in that the losses from the production of waste products are at a minimum. This, as shown hereinbefore, prevails at all conversion levels. The conventional cracking processes, however, become increasingly more inefficient at conversion levels above about 50 volume percent.

The use of hydrogen improves the performance of the conventional cracking processes. (See Table III.) Thus, at the 50 percent conversion level, the amounts of dry gas and butanes are not excessive. It is to be noted, however, that the yield of C_5+ gasoline is still low. At the 71 percent conversion level, the use of hydrogen produces a better yield of gasoline. It will also be noted, however, that the yield is little more than 60 percent of the yield achieved by the process of this invention. The production of dry gas and of butanes remains excessive, and large amounts of the charge are lost to coke. Therefore, even when hydrogen is used in the conventional cracking processes, the operation fails to achieve the efficiency and flexibility of the process of this invention.

As has been mentioned hereinbefore, the fuel oils obtained in the process of this invention are very stable and free from corrosive sulfur compounds. This will be apparent from the data set forth in Table V.

TABLE V

	Fuel Oil Properties	
	Process of Example 4	Conventional Cracking Process
Gravity, A.P.I.	46.1	30.1
ASTM Distillation:		
I.B.P. ° F.	412	355
50% ° F.	460	
E.P. ° F.	560	645
Sulfur, Wt. percent	0.006	0.1
Storage Test @ 110° F.:		
Sediment @ 6 weeks, mg.	6	110
Sediment @ 12 weeks, mg.	12	181

The storage test used to determine the tendency of a fuel oil to form sediment under storage conditions is conducted as follows:

A 500-milliliter sample of the fuel oil under test is placed in a convector oven maintained at 110° F for a period of six weeks. Then, the sample is filtered through a tared asbestos filter (Gooch crucible) to remove the insoluble matter. The weight of such matter, in milligrams, is reported as the amount of sediment. Another sample is treated in a similar manner, except that it is held in the oven for 12 weeks. At the end of that period of storage, the amount of sediment is determined, as aforedescribed.

The data in Table V show the properties of a distillate fuel oil obtained in the process of this invention, at the point of 44 percent conversion into products boiling below about 410° F., from the operation described in Example 4, using the light East Texas gas oil. The characteristics are typical of the fuel oils obtained in this process. For the purpose of comparison, the properties of a typical fuel oil obtained by the conventional cracking processes, derived from the same charge stock, are also set forth in Table V.

From the data set forth in Table V, it will be apparent to those skilled in the art that the fuel oils obtained by the process of this invention are extremely stable. On the other hand, the fuel oils produced in the conventional cracking processes have poor stability. Additionally, they contain corrosive sulfur compounds. Consequently, resort has been had to the use of various additives to stabilize these fuel oils. It will be readily appreciated that the fuel oils produced in the process of this invention do not require the use of such additives or, at most, require only small amounts of additives compared to other cracked fuel oils. In addition, as has been discussed hereinbefore, there is complete flexibility in operation to produce stable fuel oils in any yield.

The hydrogen pressure used in this invention will generally be within the range 100 to 2500 pounds per square inch gauge, and preferably within the range 350 to about 2000 pounds per square inch gauge.

In this invention, the liquid hourly space velocity, i.e., the liquid volume of hydrocarbon charge measured at 60° F. per hour per volume of catalyst, should generally be within the range about 0.1 and 10, preferbaly within the range about 0.1 to about 4. Generally, the molar ratio of hydrogen to hydrocarbon charge should be within the range about 2 to about 80, preferably within the range about 5 to about 50.

As was mentioned hereinbefore, the amount of dry gas produced in the process of this invention is small. This will be evident from the results of the runs set forth in Example 5.

EXAMPLE 5

To show amount of dry gas production

The light East Texas gas oil, described in Example 2, was subjected to the cracking process of this invention, using catalyst B. The hydrogen-to-hydrocarbon molar ratio used was 40; the liquid hourly space velocity was 0.5; and the hydrogen pressure was 1000 pounds per square inch gauge. The runs were carried out at various temperatures sufficient to effect 0–100 percent conversion into products boiling below about 410° F. (100-recycle). The pertinent data and the results of these runs are set forth in Table VI.

The three curves of Figure 6 are based upon the data set forth in Table VI. These curves show the relationship between the volume percent conversion into products boiling below about 410° F. (100-recycle), in a once-through operation, and the weight percent production, at each conversion level, of methane (curve 8), ethane (curve 9), and propane (curve 10).

It will be noted that, in a once-through operation, wherein all the gas oil charge was converted into products boiling below about 410° F., only about 0.1 weight percent of methane (curve 8), about 0.75 weight percent of ethane (curve 9), and about 2.4 weight percent of propane (curve 10) were produced. There was a total production of dry gas (C_1–C_3 hydrocarbons) not useful in gasoline, therefore, of only about 3.25 weight percent. The remainder of the products were hydrocarbons useful in gasoline. Indeed, of the 3.25 weight percent dry gas, 2.4 weight percent was propane, a gas useful in preparing liquid petroleum gas (L.P.G.), leaving only 0.85 weight percent of the charge converted into waste gases.

TABLE VI

Temp., ° F.	Vol. Percent Conversion to Products Boiling below 410° F.	Dry Gas Produced, Weight Percent		
		Methane	Ethane	Propane
640	13	0.04	0.1	0.39
685	44	0.05	0.4	1.4
690	53	0.09	0.39	1.25
705	76	0.1	0.6	1.9
745	100	0.1	0.75	2.4

It must be recognized that the production of dry gas is highest at the 100 percent conversion level. From curve A of Figure 3, it will be noted that the temperatures are highest at the highest conversion levels. At lower conversion levels, where the conditions are less severe, the total amount of dry gas produced is smaller. Therefore, even at the higher temperatures required for 100 percent conversion into products boiling below about 410° F. (100-recycle), under the conditions of pressure, space velocity, etc., used, the amount of dry gas produced is relatively small. It has been found, however, when correlating the space velocity with the temperature to effect 100 percent conversion of the charge into products boiling below about 410° F., that the weight percent of dry gas produced is less than about 10 weight percent and frequently under about 5 percent, by weight.

This may be stated in another way. At any conversion level it is desirable that, in actual commercial operation, the total dry gas made not exceed 10 percent, by weight, and preferably it should not exceed 5 percent, by weight. The catalysts specified for use in this invention are such that this limitation is easily met at commercially attractive conversion levels. In fact, the catalysts specified for use herein are such that with all charge stocks the dry gas production will not be in excess of 10 percent, by weight, and often not in excess of 5 percent, by weight, even at 100 percent conversion to products boiling below 410° F. These dry gas figures for 100 percent conversion and those of the previous paragraph will be understood to be the dry gas production at the minimum temperature necessary to convert the charge stock entirely to products boiling below 410° F. at the space velocity being used.

In the conventional cracking processes at least about 20 weight percent, and usually much more, dry gas is produced under conditions which are just severe enough to effect 100 percent conversion of the charge, in a once-through operation, into products boiling under about 410° F., i.e., gasoline and lighter products. Also, of course, large amounts of coke are formed, which makes for additional loss to the process and, of course, temperatures of 1100° F. to 1200° F. would be required just to achieve this 100 percent conversion to products boiling below 410° F. when charging heavy gas oils. Accordingly, it has not been feasible to operate conventional cracking processes at high conversion to gasoline levels, in a once-through operation.

On the other hand, as will be at once apparent to those skilled in the art, it will often be commercially feasible to operate the cracking process of this invention under conditions that effect 100 percent conversion into gasoline in a once-through operation. The amount of

dry gas produced is small and the amount of coke obtained in the process is almost negligible. Therefore, virtually all the charge stock may be converted into useful products.

The amount of dry gas produced in the process of this invention is not affected to any substantial extent by the liquid hourly space velocity. This is illustrated by the results of the runs described in Example 6.

EXAMPLE 6

Relationship between space velocity and dry gas production

The light East Texas gas oil, described in Example 2, was cracked, in a series of runs, in the presence of catalyst B. The pressure used was 1000 pounds per square inch gauge and the hydrogen-to-hydrocarbon molar ratio was 40. The runs were made at space velocities of 0.5, 1.0 and 1.5, using temperatures, at each space velocity, sufficient to achieve 0–100 percent conversion into products boiling below about 410° F. (100-recycle). Typical operating temperatures at each space velocity, and the corresponding conversions and the amounts of dry gas produced are set forth in Table VII.

TABLE VII

Temp., °F.	Space Velocity	Conversion, Vol. Percent to Products Boiling below about 410° F.	Total Dry Gas, Wt. Percent
640	0.5	13	0.4
685	0.5	45	1.82
700	0.5	68	2.3
745	0.5	100	3.25
680	1.0	18	0.5
730	1.0	55	1.9
755	1.0	80	2.75
780	1.0	100	3.4
720	1.5	32	1.4
755	1.5	60	2.1

The curve of Figure 7 is based upon the data set forth in Table VII. It was found that the relationship between the total amount of methane, ethane, and propane at each conversion level was substantially the same, regardless of the space velocity. Therefore, the curve of Figure 7 represents the relationship between the amount of dry gas produced and the amount of conversion into products boiling below about 410° F. (100-recycle) at different space velocities. It will be recognized, therefore, that the space velocity alone does not materially affect the dry gas yield. It follows that the yield of dry gas is dependent primarily on the temperature of conversion which, for catalysts in the same condition, is directly proportional to the percent conversion into products boiling below about 410° F. (100-recycle).

It has been indicated hereinbefore, however, that the temperature and the liquid hourly space velocity are the main factors affecting the degree of conversion into products boiling below about 410° F. (100-recycle). The primary effect of varying the hydrogen-to-hydrocarbon molar ratio and the hydrogen pressure is upon the amount of coke produced and on the rate of catalyst aging. Even at lower pressures and/or at lower hydrogen-to-hydrocarbon molar ratios, both as specified herein, which conditions favor increased coke formation, there is very little coke produced. It will be recognized, therefore, that the variables that must primarily be correlated, to produce high yields of gasoline and small amounts of dry gas, are the temperature and the liquid hourly space velocity. In view of the foregoing discussion, such correlation can be readily established by those skilled in the art.

As is well-known, the coke (or carbonaceous material) deposited on a cracking catalyst is usually measured in terms of the weight percent of coke based upon the weight of charge material which is contacted with a catalyst before it is regenerated, or replaced. This criterion, of course, is related to the longevity of the catalyst (i.e., its useful life before regeneration is required) and the amount of the charge which is lost to the process in the form of coke. The loss from coke formation in the process of this invention is extremely low. This is demonstrated by the run set forth in Example 7.

EXAMPLE 7

A variety of charge stocks, including high-sulfur light and medium gas oils, low-sulfur light and medium gas oils, coker gas oils, thermal gas oils, and refractory cycle stocks from a conventional cracking operation, were cracked, successively, in a continuous operation, for 133 days, using the process of this invention. Catalyst B (0.45 percent platinum on silica-alumina) was used. The hydrogen pressure employed was 1000 pounds per square gauge, the hydrogen-to-hydrocarbon molar ratio was 40, and the liquid hourly space velocity was 0.5. As each type of charge was cracked, the temperature was adjusted to effect approximately a 50 percent conversion into products boiling below about 410° F. (100-recycle). At the end of 133 days, the activity of the catalyst had dropped to a level at which regeneration was required. It was found that the amount of deposit, i.e., the gain in weight, on the catalyst was 0.005 percent, by weight, based upon the weight of charge material which had been passed over the catalyst.

It was found that about 65 percent, by weight, of the material deposited upon the catalyst was soluble in benzene. About 65 percent of the deposit, therefore, is hydrocarbonaceous, i.e., it represents adsorbed hydrocarbons. Thus, in terms of insoluble coke alone, only 35 percent of the 0.005 weight percent of the deposit on the catalyst, or about 0.002 weight percent, is coke.

It will be appreciated, therefore, that the amount of deposit on the catalyst, in the process of this invention, is negligible. In terms of insoluble coke alone, the amount of deposit on the catalyst becomes even more negligible. In a conventional cracking operation, on the other hand, the amount of coke deposited upon the catalyst, based on the weight of charge contacted with it, is 2–4 percent, by weight, and higher.

Assuming, however, that the total deposit on the catalyst, in the process of this invention, is coke, the difference between the process of this invention and the conventional cracking processes is still very pronounced. Thus, in operating a cracking unit of 10,000 barrels per calendar day capacity, the weight of the oil charged is about 3,000,000 pounds. In the cracking process of this invention, at a 50 percent conversion into gasoline, the amount of deposit on the catalyst, based on the weight of the charge, is about 150 pounds. In other words, about 150 pounds out of 3,000,000 pounds of charge is lost to the process as coke and other deposits on the catalyst. On the other hand, at similar conversions, assuming a coke deposit of 2 percent, by weight, in conventional cracking operations, the weight of charge lost to carbon, out of about 3,000,000 pounds of charge, is about 60,000 pounds.

Any hydrocarbon fraction 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 boils substantially continuously between said initial boiling point and said end boiling point, is suitable as a charge stock for the process of this invention. Such charge stocks include gas oils, residual stocks, cycle stocks which have previously been cracked in this or another cracking process, "whole topped crudes," and heavy hydrocarbon fractions derived from the destructive hydrogenation of coal, tars, pitches, asphalts, shale oils, etc., such as, for example, "middle oil." As is well-known to those skilled in the art, the distillation of higher boiling petroleum fractions (above about

750° F.) must be carried out under vacuum, in order to avoid thermal cracking. Throughout the specification and 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 which covers a variety of stocks. Throughout the specification and claims, the term, unless further modified, includes any distilled hydrocarbon fraction which is derived from crude petroleum or shale oil or the product of some process such as cracking or coking and 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 within a range falling within from about 400° F. to about 1100–1200° F., the 50 percent point being at least about 500° F.

A gas oil could boil over the entire range 400–1200° F. or it could boil over a shorter range, e.g., 500–900° F. The gas oils can be further roughly subdivided by overlapping boiling ranges. Thus, a light gas oil might boil between about 400° F. and about 600–650° F. A medium gas oil might distill between about 600–650° F. and about 700–750° F. A heavy gas oil might 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 utilizable in the process of this invention.

The refractory cycle stocks are cuts of 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.

As has been mentioned hereinbefore, the catalysts utilizable in the process of this invention, quite unexpectedly, are not deactivated by sulfur compounds, under conditions of the process. This is illustrated by the runs described in Example 8.

EXAMPLE 8

In these runs, a light gas oil distilled from a Middle East (Kuwait) crude was used. This gas oil had the following characteristics: an A.P.I. gravity of 39.1; an initial boiling point of 418° F.; a 50 percent point of 506° F.; and end point of 634° F. and a sulfur content of 0.94 percent by weight. The operating conditions employed were similar to those used in the runs described in Example 2, at the temperatures at which 50 percent conversion into products boiling below about 410° F. (100-recycle) was achieved. Catalysts E and H were employed. Using catalyst E (46.0 A.I.) at 597° F., there were obtained 0.8 weight percent dry gas (C_3 and lighter) and 49.5 volume percent C_5+ gasoline. When catalyst H (29.0 A.I.) was used at 682° F., there were obtained 1.0 weight percent dry gas and 51.5 volume percent C_5+ gasoline.

It will be noted that the temperatures for obtaining 50 percent conversion of the light Kuwait gas oil into products boiling below about 410° F. (100-recycle), using catalysts E and H, fall on curve 1 of Figure 1. The light Kuwait gas oil, however, contains a large amount of sulfur, whereas the light East Texas gas oil, which was used for obtaining the data for Figure 1, contains a small amount of sulfur. This shows that the sulfur content of the charge stock does not affect the activity of the catalyst.

The presence of even relatively small amounts of nitrogen compounds in the charge stock may interfere, to some extent, with the process of this invention. This is demonstrated by the results of the runs described in Example 9.

EXAMPLE 9

The light East Texas gas oil, described in Example 2, was hydrocracked in the presence of catalyst B. The liquid hourly space velocity used was one, the hydrogen-to-hydrocarbon molar ratio was 10, and the hydrogen pressure was 1000 pounds per square inch gauge. This run was made at 600° F. Under these operating conditions, the conversion into products boiling below about 410° F. (100-recycle) was 44 percent by volume after 3 hours of operation.

A series of runs were made under these same conditions, using catalyst B, except that various amounts of quinoline were added to the light East Texas gas oil charge, in order to increase the nitrogen content of the charge stock without altering its other properties. The nitrogen content of the charge and the volume percent conversion into products boiling below about 410° F. (100-recycle) after 3 hours of operation under the defined conditions, are set forth in Table VIII.

TABLE VIII

Wt. Percent Quinoline Added to East Texas Gas Oil	Total Nitrogen, Wt. Percent	Vol. Percent Conversion to Products Boiling Below about 410° F.
None	0.02	44
0.32	0.035	43
0.57	0.06	37
1.11	0.12	23
1.49	0.16	11

The curve presented in Figure 8 is based upon the data set forth in Table IX. This curve shows the relationship between the volume percent conversion into products boiling below about 410° F. (100-recycle), under the conditions specified in Example 9, and the nitrogen content of the charge stock after 3 hours of operation. It will be noted that as the nitrogen content increases, the conversion decreases.

The conclusion to be drawn from these data may be stated another way. For a given type of charge stock, the higher the nitrogen content, the higher will be the temperature required to effect a given amount of conversion, all other conditions being constant. Since the amount of dry gas produced is directly related to temperature, higher nitrogen contents will tend to produce somewhat higher quantities of dry gas.

Another feature of higher nitrogen contents that should be pointed out is that, all other things being constant, they require more frequent shutdown of the process of this invention to regenerate the catalyst. As the catalyst ages, the reaction temperature must be increased if the degree of conversion is to be held constant. The dry gas production increases as the temperature increases. In commercial operations, according to this invention, it is expected that this procedure of increasing the temperature to maintain conversion constant will be practiced until a temperature is reached at which the product quality and distribution are such that it is necessary to shut down and regenerate the catalyst. The principal factor in determining the point of shutdown will be excessive dry gas production which, as has been shown, is largely a function of temperature. Thus, since the initial reaction temperature for high nitrogen charge stocks will be higher than for low nitrogen charge stocks, the on-stream periods between regenerations will be shorter for high nitrogen than for low nitrogen stocks, all other conditions being equal. Thus, for long on-stream periods under severe reaction conditions, it is preferred that the nitrogen content of the feed stock be lesss than 0.10 percent, by weight, and still more preferably less than 0.08 percent, by weight. However, the process of this invention may be operated in a completely satisfactory manner with charge stocks of higher nitrogen contents.

If desired, the nitrogen content may be reduced prior to using a charge stock in the process of this invention to provide for longer periods between regenerations. The reduction in nitrogen content can be effected by any of the methods well-known in the art, such as, for example, acid treatment, propane deasphalting, and hydrogenolysis, under very high pressure, in contact with catalyst such as molybdenum or tungsten oxide, nickel sulfide, tungsten sulfide, cobalt molybdate, cobalt tungstate, etc. A higher nitrogen content can be tolerated in the charge, under more severe operating conditions, such as at higher temperatures.

The process of this invention can be carried out in any equipment suitable for carrying out catalytic operations. The process can be operated batch-wise. It is preferable, however, and most feasible, to operate continuously. Accordingly, the process can utilize a fixed bed of catalyst. It can be operated, however, using a moving bed of catalyst, wherein the hydrocarbon flow may be concurrent or countercurrent to the catalyst flow. A fluid type of operation can also be used, wherein the catalyst is carried into the reactor in suspension in the hydrocarbon charge, or fluidized with the hydrogen. Another embodiment of fluid operation applicable herein is the use of a "static" bed of catalyst, fluidized by the hydrogen gas and gaseous hydrocarbon charge.

The following examples are for the purpose of illustrating the variety of charge stocks utilizable in the process of this invention and of demonstrating the advantages thereof. It must be strictly understood, however, that this invention is not to be limited to the particular catalysts, charge stocks, or operating conditions set forth in these examples, or to the operations or manipulations involved therein.

EXAMPLE 10

A refractory cycle stock was used in this run. It was derived from a conventional cracking operation. This material is very refractory and is difficult to crack by conventional methods. It had the following properties:

A.P.I. gravity	26.3
ASTM distillation:	
I.B.P. ° F.	434
5% ° F.	466
50% ° F.	516
E.P. ° F.	650
Sulfur, wt. percent	0.48

This cycle stock was cracked at a temperature of about 671° F., using catalyst A (1.8 percent platinum deposited upon the silica-alumina carrier). The operation was carried out at a liquid hourly space velocity of one, under a hydrogen pressure of 500 pounds per square inch gauge, and using a hydrogen-to-hydrocarbon molar ratio of 8.3. Typical analyses of the products obtained are set forth in Table IX.

EXAMPLE 11

A heavy gas oil was used in this run. It was distilled from the same East Texas crude as was the light East Texas gas oil described in Example 2. It had the following properties:

A.P.I. gravity	33.2
Distillation, vacuum assay:	
I.B.P. ° F.	440
5% ° F.	489
50% ° F.	629
95% ° F.	820
Sulfur, wt. percent	0.37

This charge stock was cracked at a temperature of about 724° F., using catalyst B (0.45 percent platinum deposited upon a silica-alumina carrier). This catalyst had been in use for an extended period of time (57 days) without regeneration. The operation was carried out at a liquid hourly space velocity of 0.5, under a hydrogen pressure of 1000 pounds per square inch gauge, and using a hydrogen-to-hydrocarbon molar ratio of 40. Typical analyses of the products produced are set forth in Table IX.

EXAMPLE 12

The light Kuwait gas oil described in Example 8 was subjected to cracking, using catalyst B. This catalyst had been in service for 33 days without regeneration. The temperature employed was about 670° F., the hydrogen pressure was 1000 pounds per square inch gauge, the hydrogen-to-hydrocarbon molar ratio was 40, and the liquid hourly space velocity was 0.5. Under these conditions, there was effected a 55.2 volume percent conversion into products boiling below about 410° F. (100-recycle). After 12 days of continuous operation under these conditions, the conversion was still at the same level and the catalyst activity was unimpaired, i.e., the conversion was maintained without resort to variations in any of the afore-described conditions of operation. Typical analyses of the products are set forth in Table IX.

EXAMPLE 13

The same light Kuwait gas oil was subjected to cracking in the presence of catalyst D (0.43 percent palladium deposited upon the silica-alumina carrier). The operation was carried out at a temperature of 593° F., using a liquid hourly space velocity of one. The hydrogen pressure was 1000 pounds per square inch gauge, and the hydrogen-to-hydrocarbon molar ratio was 40. Typical analyses of the products are set forth in Table IX.

EXAMPLE 14

A heavy, high-sulfur gas oil was used in this run. It was obtained from a Kuwait crude and had the following properties:

A.P.I. gravity	31.9
Distillation, vacuum assay:	
5% ° F.	459
50% ° F.	650
95% ° F.	863
Sulfur, wt, percent	1.61

This heavy Kuwait gas oil was cracked at a temperature of about 592° F., under a hydrogen pressure of about 1000 pounds per square inch gauge, a hydrogen-to-hydrocarbon molar ratio of 40, and a liquid hourly space velocity of 0.5. The catalyst used was catalyst B (about 0.45 percent platinum on a silica-alumina base). The product distribution is set forth in Table IX.

EXAMPLE 15

The charge stock for this run was obtained by topping an East Texas crude oil to 410° F. and then subjecting it to propane deasphalting. This charge stock had the following properties:

A.P.I. gravity		30.9
Distillation, vacuum assay:		
5%	° F.	467
50%	° F.	673
95%	° F.	974
Sulfur, wt. percent		0.30

This deasphalted, topped East Texas crude was cracked at a temperature of 603° F., using catalyst B (0.45 percent platinum deposited on a silica-alumina base). The operation was conducted at a liquid hourly space velocity of 0.5, using a hydrogen-to-hydrocarbon molar ratio of 40, and under a pressure of 1000 pounds per square inch gauge. The product had the properties set forth in Table IX.

EXAMPLE 16

The charge stock for this run was an East Texas crude oil that had been topped to 410° F. It had the following properties:

A.P.I. gravity		29.9
Distillation, vacuum assay:		
5%	° F.	475
50%	° F.	675
93%	° F.	967
Sulfur, wt. percent		0.61

This charge stock, which includes tars, asphalts, etc., was cracked at 588° F., using catalyst B. The conditions of hydrogen pressure, space velocity and hydrogen-to-hydrocarbon molar ratio were the same as those set forth in Example 15. Pertinent analyses of the product are set forth in Table IX.

EXAMPLE 17

The charge stock for this run was obtained by topping a Kuwait crude oil to 410° F. and then subjecting it to propane deasphalting. This material had the following characteristics:

A.P.I. gravity		30.1
Distillation, vacuum assay:		
5%	° F.	460
50%	° F.	684
95%	° F.	958
Sulfur, wt. percent		1.78

This deasphalted, topped Kuwait crude was cracked at a temperature of 603° F., using catalyst B. The conditions of space velocity, hydrogen pressure, and hydrogen-to-hydrocarbon molar ratio were the same as those set forth in Example 15. The product distribution is set forth in Table IX.

EXAMPLE 18

A Kuwait crude was topped to 410° F. to produce a charge stock having the following properties:

A.P.I. gravity		23.0
Distillation, vacuum assay:		
5%	° F.	470
50%	° F.	734
80%	° F.	950
Sulfur, wt. percent		2.45

This charge stock, which contained all the tars, asphalts, etc., was cracked at 594° F., using catalyst B. The conditions of space velocity, hydrogen pressure, and hydrogen-to-hydrocarbon molar ratio were the same as those set forth in Example 15. The product distribution is set forth in Table IX.

TABLE IX

	Cycle Stock	Heavy East Texas Gas Oil	Kuwait Gas Oil		Heavy Kuwait Gas Oil	Deasphalted Topped East Texas Crude	Topped East Texas Crude	Deasphalted Topped Kuwait Crude	Topped Kuwait Crude
Sulfur, Wt. Percent	0.48	0.37	0.94	0.94	1.61	0.30	0.61	1.78	2.45
Catalyst	A	B	B	D	B	B	B	B	B
Temperature, ° F.	671	724	670	593	592	603	588	603	594
Conversion, Vol. Percent [1]	52.7	51.8	55.2	49.0	55.2	56.8	26.2	62.2	30.1
C_3 and Lighter, Wt. Percent	2.1	1.9	1.4	2.3	1.4	0.7	0.3	1.3	0.7
Butanes, Vol. Percent	6.3	6.8	5.5	5.4	5.5	5.1	1.9	7.3	2.9
C_5+ Gasoline, Vol. Percent	53.0	57.8	56.6	48.1	57.6	61.1	30.5	67.0	36.4
Fuel Oil, Vol. Percent	47.3	48.2	44.8	51.0	44.8	43.2	73.8	37.8	69.9

[1] Conversion into products boiling below about 410° F. (100-recycle).

Examples 10 through 12, inclusive, and 14 through 18, inclusive, show that a wide variety of charge stocks can be cracked in the process of this invention with excellent conversions. It will be noted that refractory charge stocks, such as cycle stocks (Example 10) and stocks containing substantial amounts of residual fractions (Examples 13 through 18, inclusive) can be cracked effectively by the present process. Example 13 shows that good yields and conversions are obtained when palladium instead of platinum is used as the metal in the catalyst. Examples 11 and 12 show that satisfactory operation will be obtained even after the catalyst has been aged for long periods. In all instances, the weight percent of propane and lighter gases produced is low. On the other hand, in all cases, substantial quantities of gasoline are produced. It is significant to note that the bulk of these charge stocks may be converted into materials useful in gasoline (or which can be reformed to produce high octane gasoline) or into fuel oils. Very little of the charge stock is wasted in the production of dry gas and coke. Material heavier than gasoline in the hydrocracked product, which is not desired as domestic fuel oil or which is heavier than such fuel oil, may be recycled to produce further gasoline or may be passed on to subsequent processing such as conventional catalytic cracking. The very reduced nitrogen contents of this portion of the once-through product make it an especially desirable charge stock for conventional catalytic cracking.

Example 14 shows that effective cracking is achieved even when the charge stock contains large amounts of sulful. As is well-known to those familiar with the art, charge stocks which contain about 0.5 percent sulfur, by weight, are considered to be "high-sulfur charge stocks." It has been found that such high-sulfur charge stocks, those containing 0.5 percent sulfur and much more (up

to about 3 percent), can be cracked by the process of this invention. Indeed, such stocks can be cracked without impairing the catalyst activity or efficiency for periods of six months to a year or more of continuous operation without regenerating the catalyst. If periodic regeneration is used, as required, the same catalyst can be employed for periods of several years.

Examples 14, 17 and 18, in addition to showing that the process of this invention is applicable to high-sulfur stocks, show also that it is applicable to the cracking of charge stocks that contain large amounts of sulfur and also large amounts of residual materials. In this connection, it is significant to note that the temperature required for effecting 55 percent conversion of the heavy Kuwait gas oil into gasoline products boiling below about 410° F. (100-recycle), i.e., 592° F., falls on the conversion versus temperature curve for a low-sulfur light gas oil as set forth in Figure 3. Accordingly, a 100 percent conversion of this charge stock can be achieved at temperatures similar to those required for the lighter gas oil.

Domestic fuel oils produced by this invention are very stable while the fuel oils of the prior art often are not. This was shown in Table IV. Indeed, it has been found that regardless of the charge stocks, fuel oils can be produced by the present process which are far superior in stability to those produced from the same charge stocks by the conventional cracking processes.

As stated hereinbefore, the catalysts operable in the process of this invention can include carriers other than silica alumina and promoters, such as halogens. The following examples are illustrative of these modifications:

EXAMPLE 19

The light East Texas gas oil defined in Example 2 was cracked at a temperature of about 713° F., using catalyst L (0.5 percent platinum deposited upon a carrier comprising silica-alumina and fluorine). The operation was carried out at a liquid hourly space velocity of one, under a hydrogen pressure of 1000 pounds per square inch gauge, and using a hydrogen-to-hydrocarbon molar ratio of 10. Typical analyses of the product obtained are set forth in Table X.

EXAMPLE 20

The same light East Texas gas oil was subjected to cracking at a temperature of about 717° F., using catalyst M (0.41 percent platinum supported upon an alumina-boria carrier). The operating conditions used were the same as those employed in Example 19. Typical analyses of the products obtained are set forth in Table X.

EXAMPLE 21

The light East Texas gas oil was subjected to cracking at a temperature of 664° F., using catalyst N (about 0.64 percent platinum supported upon an alumina-silica-boria carrier). The operating conditions were the same as those used in Example 19. Typical analyses of the products obtained are set forth in Table X.

TABLE X

Catalyst	East Texas Gas Oil		
	L	M	N
Temperature, ° F	713	717	664
Conversion, Vol. Percent [1]	79.4	56.8	33.0
C_3 and lighter, Wt. Percent	1.6	1.8	0.8
Butanes, Vol. Percent	5.3	6.2	2.1
C_5+ Gasoline, Vol. Percent	86.8	59.1	39.6
Fuel Oil, Vol. Percent	20.6	44.2	67.0

[1] Conversion into products boiling below about 410° F. (100-recycle)

It will be apparent from these data that catalyst carriers, other than silica-alumina, which comprise two or more refractory oxides are utilizable in the process of this invention. The catalyst can contain small amounts of a halogen and it can be composed of more than two refractory oxides. It is to be noted that effective cracking is achieved with these catalysts within the optimum temperature ranges set forth hereinbefore. However, the various catalyst carriers are not exactly equivalent. Some of the catalysts will require operating temperatures which are slightly higher or slightly lower than those required for catalysts containing a silica-alumina carrier. As has been discussed hereinbefore, the optimum operating temperature range for any given catalyst can be determined readily by those skilled in the art by plotting temperature versus conversion into products boiling below about 410° F. (100-recycle).

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to, without departing from the spirit and scope thereof, 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.

I claim:

1. A catalytic process for hydrocracking a relatively high boiling distillate 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 point of at least about 600° F., and boiling substantially continuously between said initial boiling point and said end point, into hydrocarbon products selected from the group consisting of substantially fuel oil, substantially gasoline, and a mixture of substantially gasoline and substantially fuel oil, wherein there is substantially no coke formation and the production of C_1, C_2 and C_3 gaseous hydrocarbons is less than about 10 percent by weight of said relatively high boiling petroleum hydrocarbon fraction, which comprises contacting said relatively high boiling petroleum hydrocarbon fraction with a catalyst that includes between 0.05 percent, by weight, and about 20 percent, by weight, of a metal selected from the group of metals having atomic numbers of 44 to 46, inclusive, and 76 to 78, inclusive, deposited upon a synthetic composite that has an activity index greater than 25 and which is selected from the group consisting of silica-alumina, silica-zirconia, silica-alumina-zirconia, silica-alumina-thoria, alumina-boria, silica-magnesia, silica-alumina-magnesia and silica-alumina-fluorine, at a temperature within the range about 400° F. to about 825° F.; at a hydrogen pressure, and with a net consumption of hydrogen, within the range about 100 pounds per square inch gauge to about 2500 pounds per square inch gauge, at a liquid hourly space velocity within the range about 0.1 to about 10, and at ratios of hydrogen to hydrocarbon within the range about 2 to about 80; and correlating said temperature with said liquid hourly space velocity to produce less than about 10 percent C_1, C_2 and C_3 gaseous hydrocarbons and to produce hydrocarbon products selected from the group consisting of substantially fuel oil, substantially gasoline, and a mixture of substantially gasoline and substantially fuel oil.

2. A catalytic process for hydrocracking a gas oil, having an initial boiling point of at least about 400° F., a 50 percent point of at least about 500° F., and an end point of at least about 600° F., and boiling substantially continuously between said initial boiling point and said end point, and containing less than 0.08 percent nitrogen by weight into hydrocarbon products selected from the group consisting of substantially fuel oil, substantially gasoline, and a mixture of of substantially gasoline and substantially fuel oil, wherein there is substantially no coke formation and the production of C_1, C_2 and C_3 gaseous hydrocarbons is less than about 10 percent by weight of said gas oil, which comprises contacting said gas oil with a catalyst that includes between about 0.1 percent, by weight, and about 5 percent, by weight, of platinum deposited upon a synthetic composite of silica and alumina that has an activity index of at least 28; at a temperature within the range about 500° F. to about

800° F., at a hydrogen pressure, and with a net consumption of hydrogen, within the range about 350 pounds per square inch gauge to about 2000 pounds per square inch gauge, at a liquid hourly space velocity within the range about 0.1 to about 4, and at ratios of hydrogen to hydrocarbon within the range about 5 to about 50; and correlating said temperature with said liquid hourly space velocity to produce less than about 10 percent C_1, C_2 and C_3 gaseous hydrocarbons and to produce hydrocarbon products selected from the group consisting of substantially fuel oil, substantially gasoline, and a mixture of substantially gasoline and substantially fuel oil.

3. A catalytic process for hydrocracking a gas oil having an initial boiling point of at least about 400° F., a 50 percent point of at least about 500° F., and an end point of at least about 600° F., and boiling substantially continuously between said initial boiling point and said end point, and containing less than about 0.08 percent nitrogen, by weight, into substantially fuel oil, wherein there is substantially no coke formation and substantially no production of C_1, C_2 and C_3 gaseous hydrocarbons, which comprises contacting said gas oil with a catalyst that includes between about 0.1 percent, by weight, and about 5 percent, by weight, of platinum supported upon a silica-alumina carrier that has an activity index of at least about 28, at a temperature within the range about 500° F. to about 800° F., at a hydrogen pressure, and with a net consumption of hydrogen, within the range about 350 pounds per square inch gauge to about 2000 pounds per square inch gauge, at a liquid hourly space velocity within the range about 0.1 to about 4, and at ratios of hydrogen to hydrocarbon charge within the range about 5 to about 50; and correlating said temperature with said liquid hourly spaced velocity to produce substantially no C_1, C_2 and C_3 gaseous hydrocarbons and to produce substantially fuel oil.

4. A catalytic process for hydrocracking a gas oil having an initial boiling point of at least about 400° F., a 50 percent point of at least about 500° F., and an end point of at least about 600° F., and boiling substantially continuously between said initial boiling point and said end point, and containing less than about 0.08 percent nitrogen, by weight, into substantially gasoline, wherein there is substantially no coke formation and the production of C_1, C_2 and C_3 gaseous hydrocarbons is less than about 10 percent by weight of said gas oil, which comprises contacting said gas oil with a catalyst that includes between about 0.1 percent, by weight, and about 5 percent, by weight, of platinum supported upon a silica-alumina carrier that has an activity index of at least about 28, at a temperature within the range about 500° F. to about 800° F., at a hydrogen pressure, and with a net consumption of hydrogen, within the range about 350 pounds per square inch gauge to about 2000 pounds per square inch gauge, at a liquid hourly space velocity within the range about 0.1 to about 4, and at ratios of hydrogen to hydrocarbon within the range about 5 to about 50; and correlating said temperature with said liquid hourly space velocity to produce less than about 10 percent C_1, C_2 and C_3 gaseous hydrocarbons and to produce substantially gasoline.

5. A catalytic process for hydrocracking a gas oil, having an initial boiling point of at least about 400° F., a 50 percent point of at least about 500° F., and an end point of at least about 600° F., and boiling substantially continuously between said initial boiling point and said end point, and containing less than about 0.08 percent nitrogen, by weight, into hydrocarbon products selected from the group consisting of substantially fuel oil, substantially gasoline, and a mixture of substantially gasoline and substantially fuel oil, wherein there is substantially no coke formation and the production of C_1, C_2 and C_3 gaseous hydrocarbons is less than about 10 percent by weight of said gas oil, which comprises contacting said gas oil with a catalyst that includes between about 0.1 percent, by weight, and 5 percent, by weight, of palladium deposited upon a synthetic composite of silica and alumina that has an activity index greater than 25, at a temperature within the range about 500° F. to about 800° F., at a hydrogen pressure, and with a net consumption of hydrogen, within the range about 350 pounds per square inch gauge to about 2000 pounds per square inch gauge, at a liquid hourly space velocity within the range about 0.1 to about 4, and at ratios of hydrogen to hydrocarbon within the range about 5 to about 50; and correlating said temperature with said liquid hourly space velocity to produce less than about 10 percent C_1, C_2 and C_3 gaseous hydrocarbons and to produce hydrocarbon products selected from the group consisting of substantially fuel oil, substantially gasoline, and a mixture of substantially gasoline and substantially fuel oil.

6. A catalytic process for hydrocracking a distillate petroleum 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 point of at least about 600° F., and boiling substantially continuously between said initial boiling point and said end point and containing less than 0.1 percent nitrogen, by weight, into hydrocarbon products selected from the group consisting of substantially fuel oil, substantially gasoline and a mixture of substantially gasoline and substantially fuel oil, wherein there is substantially no coke formation and the production of C_1, C_2 and C_3 gaseous hydrocarbons is less than about 10 percent by weight of said distillate fraction, which comprises contacting said distillate fraction with a catalyst that includes between about 0.1 percent, by weight, and about 5 percent, by weight, of platinum deposited upon a synthetic composite of silica and alumina that has an activity index of at least 28; at a temperature within the range about 500° F. to about 800° F.; at a hydrogen pressure, and with a net consumption of hydrogen, within the range about 350 pounds per square inch gauge to about 2000 pounds per square inch gauge, at a liquid hourly space velocity within the range about 0.1 to about 4, and at ratios of hydrogen to hydrocarbon within the range about 5 to about 50; and correlating said temperature with said liquid hourly space velocity to produce less than about 10 percent C_1, C_2 and C_3 gaseous hydrocarbons and to produce hydrocarbon products selected from the group consisting of substantially fuel oil, substantially gasoline, and a mixture of substantially gasoline and substantially fuel oil.

7. A catalytic process for hydrocracking a cycle stock, having an initial boiling point of at least about 400° F., a 50 percent point of at least about 500° F., and an end point of at least about 600° F., and boiling substantially continuously between said initial boiling point and said end point and containing less than 0.08 percent nitrogen, by weight, into hydrocarbon products selected from the group consisting of substantially fuel oil, substantially gasoline, and a mixture of substantially gasoline and substantially fuel oil, wherein there is substantially no coke formation and the production of C_1, C_2 and C_3 gaseous hydrocarbons is less than about 10 percent by weight of said cycle stock, which comprises contacting said cycle stock with a catalyst that includes between about 0.1 percent, by weight, and about 5 percent, by weight, of platinum deposited upon a synthetic composite of silica and alumina that has an activity index of at least 28; at a temperature within the range about 500° F. to about 800° F., at a hydrogen pressure, and with a net consumption of hydrogen, within the range about 350 pounds per square inch gauge to about 2000 pounds per square inch gauge, at a liquid hourly space velocity within the range about 0.1 to about 4, and at ratios of hydrogen to hydrocarbon within the range about 5 to about 50; and correlating said temperature with said liquid hourly space velocity to produce less than about 10 percent C_1, C_2 and C_3 gaseous hydrocarbons and to produce hydrocarbon products selected from the group

consisting of substantially fuel oil, substantially gasoline, and a mixture of substantially gasoline and substantially fuel oil.

8. A catalytic process for hydrocracking a gas oil, having an initial boiling point of at least about 400° F., a 50 percent point of at least about 500° F., and an end point of at least about 600° F., and boiling substantially continuously between said initial boiling point and said end-point and containing less than 0.08 percent nitrogen, by weight, into hydrocarbon products selected from the group consisting of substantially fuel oil, substantially gasoline, and a mixture of substantially gasoline and substantially fuel oil, wherein there is substantially no coke formation and the production of C_1, C_2 and C_3 gaseous hydrocarbons is less than about 10 percent by weight of said gas oil, which comprises contacting said gas oil with a catalyst that includes between about 0.1 percent, by weight, and about 5 percent, by weight, of platinum deposited upon a synthetic composite of silica, alumina, and fluorine that has an activity index of at least 28; at a temperature within the range about 500° F. to about 800° F., at a hydrogen pressure, and with a net consumption of hydrogen, within the range about 350 pounds per square inch gauge to about 2000 pounds per square inch gauge, at a liquid hourly space velocity within the range about 0.1 to about 4, and at ratios of hydrogen to hydrocarbon within the range about 5 to about 50; and correlating said temperature with said liquid hourly space velocity to produce less than about 10 percent C_1, C_2 and C_3 gaseous hydrocarbons and to produce hydrocarbon products selected from the group consisting of substantially fuel oil, substantially gasoline, and a mixture of substantially gasoline and substantially fuel oil.

9. A catalytic process for hydrocracking a relatively high-boiling distillate 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 point of at least about 600° F., and boiling substantially continuously between said initial boiling point and said end point, into hydrocarbon products wherein there is substantially no coke formation and the production of C_1, C_2 and C_3 gaseous hydrocarbons is less than about 10 percent by weight of said relatively high boiling petroleum hydrocarbon fraction, which comprises contacting said relatively high boiling hydrocarbon fraction with a catalyst that includes between 0.05 percent, by weight, and about 20 percent, by weight, of a metal selected from the group of metals having atomic numbers of 44 to 46, inclusive, and 76 to 78, inclusive, deposited upon a synthetic composite that has an activity index greater than 25 and which is selected from the group consisting of silica-alumina, silica-zirconia, silica-alumina-zirconia, silica-alumina-thoria, alumina-boria, silica-magnesia, silica-alumina-magnesia, and silica-alumina-fluorine, said composite at a temperature within the range about 400° F. to about 825° F.; at a hydrogen pressure, and with a net consumption of hydrogen, within the range about 100 pounds per square inch gauge to about 2500 pounds per square inch gauge, at a liquid hourly space velocity within the range about 0.1 to about 10, and at ratios of hydrogen to hydrocarbon within the range about 2 to about 80; and correlating said temperature with said liquid hourly space velocity to produce less than about 10 percent C_1, C_2 and C_3 gaseous hydrocarbons.

10. A catalytic process for hydrocracking a distillate petroleum 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 point of at least about 600° F., and boiling substantially continuously between said initial boiling point and said end point and containing less than about 0.1 percent nitrogen, by weight, into hydrocarbon products, wherein there is substantially no coke formation and the production of C_1, C_2 and C_3 gaseous hydrocarbons is less than about 10 percent, by weight, of said distillate fraction, which comprises contacting said distillate fraction with a catalyst that includes between about 0.1 percent by weight, and about 5 percent, by weight, of platinum deposited upon a synthetic composite of silica and alumina that has an activity index of at least 28; at a temperature within the range about 500° F. to about 800° F.; at a hydrogen pressure, and with a net consumption of hydrogen, within the range about 350 pounds per square inch gauge to about 2000 pounds per square inch gauge, at a liquid hourly space velocity within the range about 0.1 to about 4, and at ratios of hydrogen to hydrocarbon within the range about 5 to about 50; and correlating said temperature with said liquid hourly space velocity to produce less than about 10 percent C_1, C_2 and C_3 gaseous hydrocarbons.

11. A process for hydrocracking 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 point of at least about 600° F., which comprises contacting said hydrocarbon fractions with a catalyst that includes between about 0.05 percent, by weight, and about 20 percent, by weight, of at least one metal selected from the group consisting of metals having atomic numbers of 44 to 46, inclusive, and 76 to 78, inclusive, deposited upon a synthetic composite that has an activity index greater than 25 and which is selected from the group consisting of silica-alumina, silica-zirconia, silica-alumina-zirconia, silica-alumina-thoria, alumina-boria, silica-magnesia, silica-alumina-magnesia, and silica-alumina-fluorine at a temperature within the range about 400° F. to about 825° F.; at a liquid hourly space velocity within the range about 0.1 to about 10; in the presence of hydrogen, and with a net consumption of hydrogen, under hydrogen pressures within the range about 100 pounds per square inch gauge to about 2500 pounds per square inch gauge and using a molar ratio of hydrogen to hydrocarbon charge within the range about 2 to about 80; and controlling said reaction conditions to produce an amount of dry gas less than 10 percent by weight of said hydrocarbon fraction during said hydrocracking.

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