

Nov. 24, 1959

F. G. CIAPETTA

2,914,461

HYDROCRACKING OF A HIGH BOILING HYDROCARBON OIL
WITH A PLATINUM CATALYST CONTAINING ALUMINA
AND AN ALUMINUM HALIDE

Filed Nov. 9, 1954

2 Sheets-Sheet 1

Fig. 1

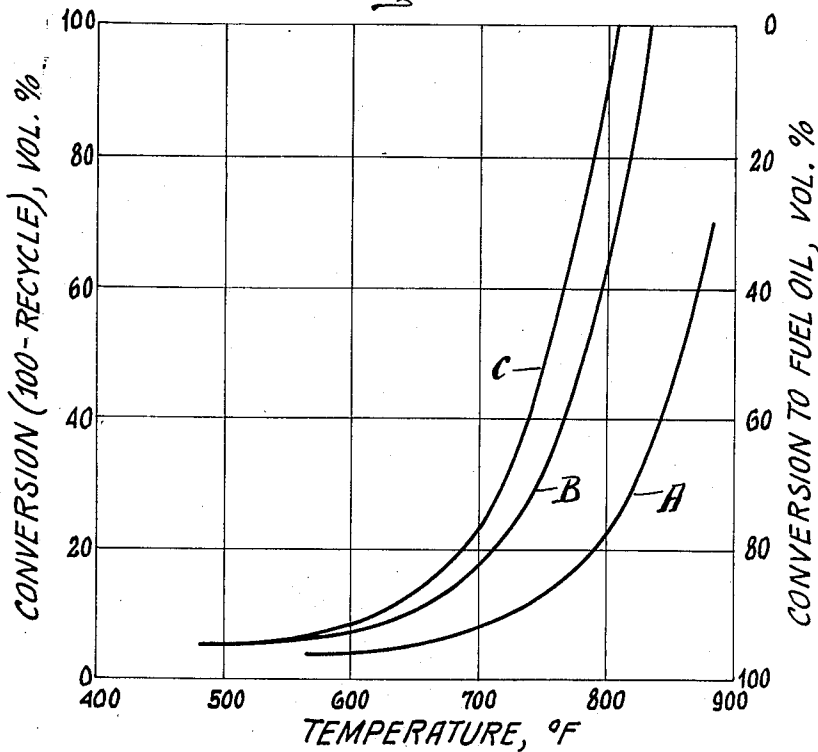
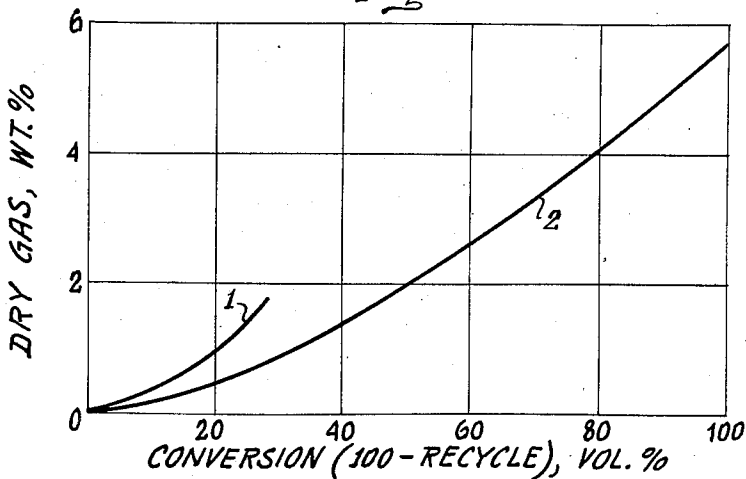


Fig. 2



INVENTOR
Frank G. Ciapetta
BY
Hastings S. Trigg
ATTORNEY

Nov. 24, 1959

F. G. CIAPETTA

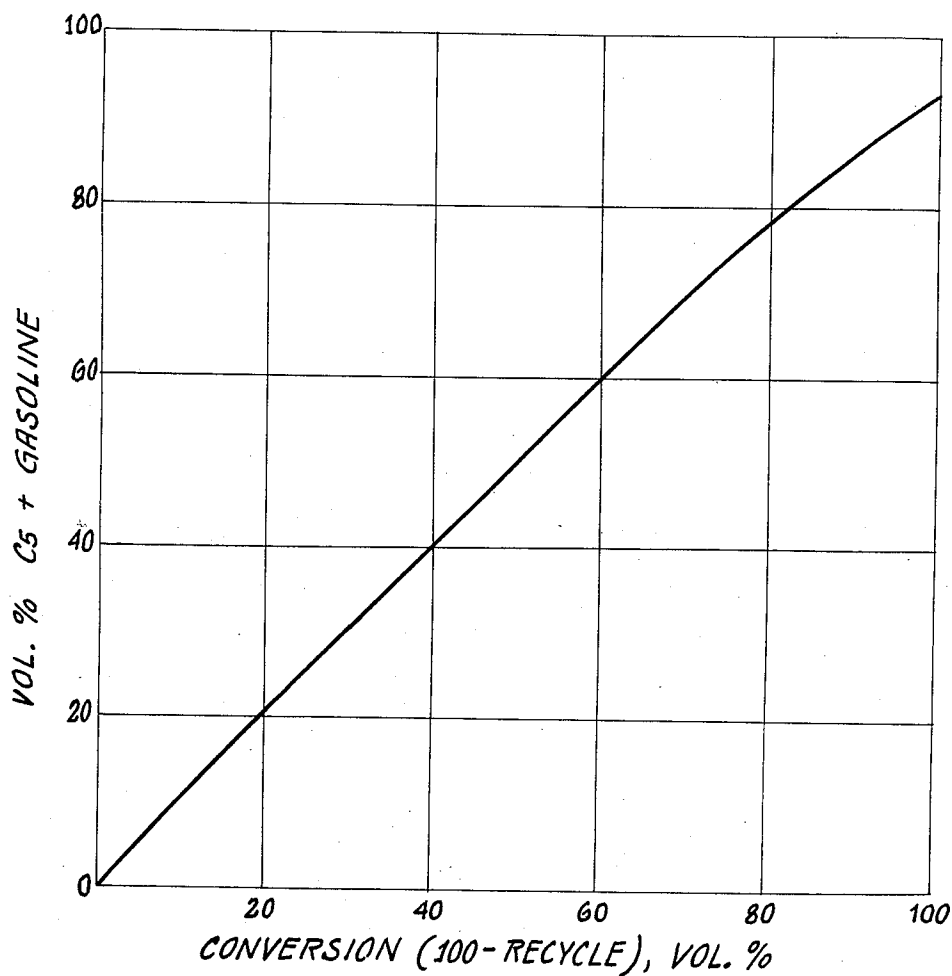
2,914,461

HYDROCRACKING OF A HIGH BOILING HYDROCARBON OIL
WITH A PLATINUM CATALYST CONTAINING ALUMINA
AND AN ALUMINUM HALIDE

Filed Nov. 9, 1954

2 Sheets-Sheet 2

Fig. 3



INVENTOR

Frank G. Ciapetta

BY

Hastings S. Trigg

ATTORNEY

1

2,914,461

HYDROCRACKING OF A HIGH BOILING HYDRO-CARBON OIL WITH A PLATINUM CATALYST CONTAINING ALUMINA AND AN ALUMINUM HALIDE

Frank G. Ciapetta, Upper Darby, Pa., assignor to Socony Mobil Oil Company, Inc., a corporation of New York

Application November 9, 1954, Serial No. 467,836

3 Claims. (Cl. 208—111)

This invention relates to the catalytic cracking of petroleum hydrocarbon stocks. It is more particularly concerned with a process wherein relatively high-boiling petroleum hydrocarbon fractions are subjected to cracking in the presence of supported platinum or palladium catalysts, to produce useful hydrocarbons boiling within the gasoline range.

As is well known to those skilled in the art, cracking is a general term applied to operations wherein mixtures of hydrocarbon molecules of 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 use of temperatures of such magnitude is disadvantageous, however, because of the production of coke and of relatively large amounts of dry gas (methane, ethane, ethylene, propylene, and propane) and of excess amounts of 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. A part from the losses in yield caused by the formation of coke and dry gas, the use of elevated temperatures is undesirable from the standpoint of the economics of the operation, as those familiar with the art will readily appreciate.

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 light gases produced. As a consequence, the supply of available cracking stocks has been restricted.

Even cycle stocks obtained from the catalytic cracking of non-refractory petroleum cracking stocks are not satisfactory charge stocks, because large amounts of coke and light gases are produced. Accordingly, it has been the practice to process the cycle stocks in separate operations, such as by thermal cracking. The many disadvantages of this type of operation, however, will be readily appreciated by those skilled in the art.

When cracking operations are carried out in the presence of hydrogen at relatively high temperatures and under high pressures, i.e., conventional hydrocracking, the aforescribed limitations on the type of charge stocks are not generally applicable. Thus, cycle stocks, heavy residuals, etc. can be cracked in hydrocracking operations. Conventional hydrocracking, however, has 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

2

of expensive, high-pressure equipment. Another undesirable characteristic of the hydrocracking processes of the prior art has had to do with sulfur-containing stocks. These stocks cannot be used in hydrocracking operations, unless special catalysts are employed.

Charge stocks otherwise suitable for catalytic cracking operations may contain, however, relatively large amounts of sulfur. The presence of sulfur has necessitated the use of special "sulfur-resistant" catalysts, because many cracking catalysts are rendered ineffective, i.e., "poisoned," by sulfur. Accordingly, metallic hydrogenation catalysts have not been used, because of the relative ease with which they become poisoned. Insofar as is now known, therefore, the use of platinum or palladium catalysts in cracking operations has never been proposed.

Accordingly, it will be appreciated that the provision of a catalytic cracking process involving relatively low temperatures, which is flexible from the standpoint of the production of useful products, with low dry gas and coke production, 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 and the sulfur-containing charge stocks, can be catalytically cracked in the presence of novel catalysts to produce excellent yields of hydrocarbons boiling in the gasoline range. It has now been discovered that the catalytic cracking of such charge stocks can be readily effected when the operation is carried out in the presence of hydrogen and of a catalyst comprising a metal of the platinum or palladium series deposited upon a synthetic composite of a metal oxide and a metal halide of a refractory nature.

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 petroleum charge stocks to produce gasoline and/or fuel oil in excellent yields. A further object is to provide a process for effecting cracking of petroleum charge stocks at relatively low temperatures and pressures. A still 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 cracking petroleum charge stocks, in the presence of hydrogen and of catalysts comprising metals of the platinum and palladium series deposited upon a synthetic composite of a refractory metal oxide and a metal halide. A further specific object is to provide a process for cracking refractory charge stocks such as cycle stocks derived from the cracking of non-refractory charge stocks. Another specific object is to provide a process for cracking sulfur-containing petroleum charge stocks. A further specific object is to provide a process for cracking a wide variety of petroleum charge stocks to produce excellent yields of gasoline, with a minimum production of dry gas and coke, and with a maximum production of liquid products, without poisoning the catalyst. A still further specific object is to provide a process for converting a wide variety of petroleum 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 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 fol-

lowing detailed description considered in conjunction with the figures, wherein:

Figure 1 presents a series of curves showing graphically the relationship between the temperature and the volume percent conversion into products boiling below about 410° F. (100-recycle), and the volume percent conversion into fuel oil, obtained by cracking a typical gas oil in the presence of typical catalysts of this invention and of a catalyst that is outside this invention;

Figure 2 presents a series of curves showing graphically the relationship between the volume percent conversion into products boiling below about 410° F. (100-recycle) and the yield of dry gas obtained by cracking a typical gas oil in the presence of typical catalysts of this invention and of a catalyst that is outside this invention; and

Figure 3 presents a curve showing graphically the relationship between the volume percent yield of products boiling below about 410° F. (100-recycle) and the volume percent yield of C₅₊ gasoline, obtained by cracking a typical gas oil by means of the process of this invention.

Broadly stated, the present invention provides a process for cracking petroleum charge stocks to produce gasoline and/or fuel oil, which comprises contacting a petroleum 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, in the presence of hydrogen in amounts varying, on the basis of the molar ratio of hydrogen to hydrocarbon charge, between about 2 and about 80, with a catalyst comprising between about 0.05 percent and about 20 percent, by weight of the catalyst, of at least one metal of the platinum and palladium series deposited upon a synthetic composite of alumina or silica with an aluminum halide, said composite having an activity index of at least about 30, under hydrogen pressures varying between about 100 pounds per square inch gauge and about 2500 pounds per square inch gauge, at a liquid hourly space velocity of between about 0.1 and about 10, and at a temperature varying between about 400° F. and about 850° F.

Throughout the specification and in the claims, the term "C₅₊ 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), of gasoline or of fuel oil obtained in the process of this invention. It is expressed in terms of the 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 recycle stock (fuel oil) from 100 percent, i.e., from the initial volume of the charge. The expression "(100-recycle)" is an abbreviation for 100 percent minus the volume percent recycle. As is discussed hereinafter, all the cycle stock (i.e., effluent boiling above about 410° F.) is excellent fuel oil. Accordingly, conversion into fuel oil is the volume percent of product which boils above about 410° F. Conversion to C₅₊ gasoline is the volume percent of product boiling between about 60° F. and about 410° F. The volume percent of conversion into products boiling below about 410° F. (100 recycle) and the volume percent of conversion into fuel oil totals to 100 volume percent, based upon the initial charge. "Dry gas" refers to the methane, ethane, propane, and ethylene and propylene produced in a cracking process, expressed in terms of weight percent of the initial charge. The cracking activity of a carrier is expressed in terms of the percent, by volume, of a standard hydrocarbon charge which is cracked, under specific operating conditions, in the "Cat. A" test. This test is described by Alexander and Shimp in National

Petroleum News, 36, page R-537 (August 2, 1944). The unit for rating the cracking activity of a material is called the "Activity Index" (A.I.).

The synthetic composites of a refractory oxide and of a metal halide that are contemplated as carriers or supports for the catalysts utilizable herein are composites of alumina with an aluminum halide and of silica with an aluminum halide. Non-limiting examples of such carriers are silica-aluminum fluoride, silica-aluminum chloride, alumina-aluminum fluoride, and alumina-aluminum chloride. The content of aluminum halide in the carrier varies between about 3 percent, by weight, and about 20 percent, by weight. In order to achieve effective cracking with low yields of dry gas, however, it has been found that the carrier must have an activity index of at least about 30, ordinarily between about 30 and about 52. Preferably, the Activity Index should be between about 35 and about 52.

The carriers can be produced by any of the methods known to the art. The following illustrative methods can be used, with suitable modification, to prepare the carriers contemplated herein. Silica-aluminum fluoride can be prepared by compositing, e.g., by ball-milling, silica hydrogel with aluminum fluoride in the required proportions. Aluminum fluoride can be obtained from any suitable source, such as, for example, by treating alumina hydrogel with hydrogen fluoride. The composite of alumina with aluminum fluoride can be prepared by ball-milling alumina hydrogel and aluminum fluoride in suitable proportions. Another procedure involves treating alumina hydrogel or a calcined alumina with an aqueous solution containing a sufficient amount of soluble fluorine compound, e.g., ammonium fluoride, hydrogen fluoride, etc., to produce the amount of aluminum fluoride desired in the final composite. If it is desired, the composites can be shaped, as by pelleting or by extrusion techniques. The composite is dried at about 220° F. and, finally, calcined in air at 900-1400° F.

The amount of metal of the platinum or palladium series deposited upon the carrier will vary between about 0.05 percent, by weight, and about 20 percent, by weight, of the final catalyst, preferably, between about 0.1 percent and about 5 percent. The metals of the platinum and the palladium series are those having atomic numbers of 44-46, and 76-78. 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 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), then treated with hydrogen at elevated temperatures (about 400° F. to about 500° F. for about 2 to 4 hours) to reduce the chloride to the metal and to activate the catalyst. Another method involves depositing the metal upon the carrier in the form of the metal sulfide. The composite is then oxidized with air to remove the sulfur and finally activated in hydrogen at elevated temperatures. Prior to use in the process, the catalyst is further activated in a hydrogen atmosphere at temperatures of about 900° F. to about 1100° F., for about 2 hours to about 16 hours.

After the catalyst has been in service for a substantial period of time, reactivation of the catalyst may be neces-

sary. 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 900° 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 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 2 to 10 hours to complete reactivation.

As has been mentioned hereinbefore, the content of aluminum halide in the catalyst support must be at least 3 percent, in order to effect cracking with low yields of dry gas. This is illustrated by the following examples:

EXAMPLE 1

Catalysts comprising platinum on alumina-aluminum fluoride carriers were prepared as follows:

Three alumina-aluminum fluoride carriers, having different contents of aluminum fluoride, were prepared. In each case, commercial activated alumina granules were covered with an aqueous solution containing a sufficient concentration of ammonium fluoride to produce the desired amount of aluminum fluoride in the finished carrier, and permitted to stand for about one hour. Each carrier was dried at about 280° F. for about 16 hours, and calcined in air for about 3 hours at 1100° F.

The carriers thus prepared were crushed to pass through a 14-mesh screen and the material retained on a 25-mesh screen (U.S. standard screen series) was used for catalyst preparation. Each carrier was sprayed with 0.066 molar aqueous solution of chloroplatinic acid, in order to deposit sufficient chloroplatinic acid on the carrier to achieve a final platinum content of about 0.5 weight percent. The thus-impregnated carrier was heated for 18 hours at 230° F., in a covered vessel, and then cooled to room temperature. Subsequently, the carrier was heated from 80° F. to about 450° F. during a 2-hour period, in the presence of nitrogen which was passed through it at a rate of 1 cc. per cubic centimeter of carrier per minute. When the temperature reached 450° F., the nitrogen stream was replaced with a hydrogen stream (at the same flow rate), and heating was continued at 450° F. for two hours. Then, the temperature was raised to 950° F. and maintained at this level for 2 hours, in order to complete the activation of the catalysts.

The catalysts (A, B, and C) prepared as aforescribed had the properties set forth in Table I.

Table I

Catalyst.....	A	B	C
Platinum, Wt. Percent.....	0.54	0.54	0.53
AlF ₃ , Wt. Percent.....	1.4	3.4	4.86
Activity Index.....	26.4	37.3	39.3

EXAMPLE 2

The charge stock used in the runs described in this example was a light gas oil that had been distilled from an East Texas crude oil. This light East Texas gas oil had the following properties:

Gravity, A.P.I.	37.5
ASTM distillation:	
I.B.P. ° F..	416
50% ° F..	516
E.P. ° F..	622
Sulfur, wt percent	0.14

This gas oil was subjected to cracking at several temperatures, using catalyst A. The operation was carried out at a liquid hourly space velocity of 1, under a hydrogen pressure of 1000 pounds per square inch gauge, and using a hydrogen to hydrocarbon molar ratio of 10. Similar operations, under the same conditions, were carried out using catalysts B and C. The pertinent data and product distribution for these runs are set forth in Table II.

The curves presented in Figures 1, 2, and 3 are based upon the data set forth in Table II. In Figure 1, curves A, B, and C present graphically the relationship between the temperature and the volume percent conversion into products boiling below about 410° F. (100-recycle) and into fuel oil when cracking is carried out using catalysts A, B, and C, respectively. It will be noted that high conversion into products boiling below 410° F. (100-recycle) can be achieved at relatively low temperatures, when catalysts having an A.I. of at least 35 and containing at least 3 weight percent aluminum fluoride (catalysts B and C) are used. On the other hand, catalyst A (having an A.I. of less than 35 and an aluminum fluoride content of less than 3 percent) does not effect much conversion even at relatively high temperatures. More significantly, the amount of dry gas produced using a catalyst having an A.I. and an aluminum halide content that are too low is excessive. This is illustrated in Figure 2.

The curves presented in Figure 2 are based upon data from Table II and show graphically the relationship between the volume percent conversion into products boiling below 410° F. (100-recycle) and into fuel oil and the weight percent yield of dry gas, in cases in which cracking is carried out in the presence of catalysts having various aluminum halide-contents. Curve 1 presents this relationship in cases in which the catalyst used contains less than 3 weight percent aluminum halide and has an A.I. of less than 35 (catalyst A). Curve 2 presents this relationship for catalysts having at least 35 A.I. and containing 3 weight percent aluminum halide (catalysts B and C). It is to be noted (curve 2) that, in the case of catalysts B and C, even at a 100 percent-conversion level, the amount of dry gas produced is less than 6 weight percent. On the other hand, in the case in which the catalyst contains less than 3 weight percent aluminum halide (curve 1), the yield of gasoline, at the 100 percent-conversion level, is very low, because of the amount of dry gas produced. The catalysts that are utilizable in the process of this invention, therefore, must have activity indices of at

Table II

Temperature, ° F.....	Runs Using Catalyst A						Runs Using Catalyst B						Runs Using Catalyst C					
	499	599	651	698	747	797	501	603	654	699	751	801	504	604	653	700	761	814
Conversion to products boiling below 410° F., Vol. Percent.....	7.3	4.3	5.7	8.8	9.8	23.7	6.4	8.1	10.1	16.8	33.1	69.9	4.6	7.7	15.7	22.9	60.2	87.0
Fuel Oil (Recycle), Vol. Percent.....	92.7	95.7	94.3	91.2	90.2	76.3	93.6	91.9	89.9	83.2	66.9	30.1	95.4	92.3	84.3	77.1	39.8	13.0
Dry Gas, Wt. Percent.....	0.2	0.2	0.3	0.3	0.3	1.5	0.1	0.1	0.3	1.1	3.2	0.3	0.3	0.3	0.4	2.6	4.7	4.7
Butanes, Vol. Percent.....	0.9	0.1	0.1	0.4	1.2	0.6	0.6	0.1	0.6	1.8	7.4	0.5	0.5	0.8	1.2	5.7	12.9	12.9
C ₅ + Gasoline, Vol. Percent.....	5.9	3.8	6.5	6.5	8.9	21.6	5.4	8.6	8.9	16.4	36.1	69.6	4.5	9.1	16.7	23.3	59.8	83.1

NOTE.—All runs at 1,000 p.s.i.g.; 1 L.H.S.V.; 10 H₂/oil molar ratio.

least about 35 and must contain at least 3 weight percent of an aluminum halide.

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 within the ranges set forth herein to effect a 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. Accordingly, as will be at once apparent to those skilled in the art, it is commercially feasible to operate the cracking process of this invention under conditions that effect a 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 negligible. Therefore, virtually all the charge stock is converted into useful products.

Cracking in accordance with the process of this invention is carried out at relatively low temperatures. This is illustrated by curves B and C in Figure 1. From these curves, it will be noted that high conversions into products boiling below about 410° F. (100-recycle) (over 50%) are effected at temperatures of about 750° F. to 800° F. Substantial conversions into products boiling below 410° F. are achieved, however, at temperatures as low as about 650° F. Complete conversion into substantially fuel oil occurs at about 400° F. The precise range of temperatures operable for a given catalyst will vary somewhat depending upon the particular metal, the activity index of the carrier, and the age of the catalyst. Generally, however, conversion, in accordance with this invention, into products boiling below about 410° F. (100-recycle) which are substantially gasoline, or into substantially fuel oil, or into both, is effected at temperatures varying between about 400° F. and about 850° F. Preferred operation is carried out at temperatures varying between about 650° F. and about 850° F.

The range of operating temperatures for the process of this invention will vary also depending upon the space velocity employed and upon whether the catalyst is freshly prepared or aged, i.e. "stabilized." In general, however, it is not feasible to operate at temperatures substantially in excess of about 850° F.

Another outstanding feature of the process of this invention will also be apparent from the curves shown in Fig. 1 and from the data set forth in Table I. This is the complete flexibility of the ratio between the production of products boiling below about 410° F. (100-recycle) and of distilled fuel oil. The product boiling below about 410° F. is substantially all gasoline, as most of the butanes produced are used with the C₅₊ gasoline to meet vapor pressure requirements. The material boiling above about 410° F. is a good recycle stock. This material, however, is an excellent distillate fuel oil too. This fuel oil has a high hydrogen to hydrocarbon ratio and has an end-point much lower than the end-point of the initial charge stock. It has also been found that this fuel oil has excellent storage stability characteristics without necessitating resort to stabilizing additives. It is to be noted from curves B and C in Fig. 1 that, depending upon the temperature of operation, other conditions being constant, it is possible to produce substantially gasoline and fuel oil in any ratios. Thus, when operating at lower temperatures, substantially all the charge stock can be converted into fuel oil. When operating at higher temperatures, on the other hand, substantially all the charge stock can be converted into substantially gasoline. When operating at intermediate temperatures, any ratio of fuel oil to substantially gasoline can 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 the curves in Fig. 1. Insofar as

is now known, such flexibility of operation has not been possible with the processes of the prior art.

The curve set forth in Fig. 3 presents graphically the relationship between the volume percent conversion into products boiling below 410° F. (100-recycle) and the volume percent of C₅₊ gasoline that is produced, when cracking is carried out, in accordance with this invention, in the presence of catalyst C. This curve is based upon data set forth in Table II. It will be noted that the amount of C₅₊ gasoline produced at any given conversion level is high. It will be appreciated, therefore, that virtually all the material that is converted into products boiling below about 410° F. (100-recycle) is gasoline. A very small amount is converted into dry gas and excess butanes.

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

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). When higher space velocities are used, somewhat higher temperatures are required. The primary effect of varying the hydrogen to hydrocarbon molar ratio and the hydrogen pressure is upon the amount of coke produced. 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 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.

Any 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, is suitable as a charge stock for the process of this invention. Such charge stocks include gas oils, residual stocks, cycle stocks, "whole topped crudes," and heavy hydrocarbon fractions derived by the destructive hydrogenation of coal, tars, pitches, asphalts, etc., such as, for example, "middle oil." As is well known to those skilled in the art, the distillation of higher-boiling petroleum fractions (above about 750° F.) must be carried out under vacuum, in order to avoid thermal cracking. Throughout the specification and in the claims, however, the boiling temperatures are expressed in terms of the boiling point at atmospheric pressure. In other words, in all instances, the boiling points of fractions distilled under vacuum have been corrected to the boiling points at atmospheric pressure. As is well known to those familiar with the art, the term "gas oil," is a broad, general term which covers a variety of stocks. Throughout the specification and in the claims, the term, unless further modified, includes any fraction distilled from petroleum which has an initial 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 boil-

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

As mentioned hereinbefore, a residual stock is any fraction which is not distilled. Therefore, any fraction, regardless of its initial boiling point, which includes all the heavy bottoms, such as tars, asphalts, etc., is a residual fraction. Accordingly, a residual stock can be the portion of the crude remaining undistilled at 1100–1200° F., or it can be made up of a gas oil fraction plus the portion undistilled at 1100–1200° F. A "whole topped crude," as the name implies, is the entire portion of the crude remaining after the light ends (the portion boiling up to about 400° F.) have been removed by distillation. Therefore, such a fraction includes the entire gas oil fraction (400° F. to 1100–1200° F.) and the undistilled portion of the crude petroleum boiling above 1100–1200° F. If it is desired, the residual fractions and the whole topped crude can be deasphalted by any means known to the art. Such treatment, however, is not necessary for charge stocks 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 40° 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 the conditions of the process.

The presence of even relatively small amounts of nitrogen compounds in the charge stock interferes with the process of this invention. For relatively short terms of operation, the presence of nitrogen in amounts of as much as about 0.12 percent, by weight, and higher can be tolerated in the charge. When operating with such charge stocks, however, it is necessary to resort to intermittent operation.

Charge stocks that contain about 0.1 percent nitrogen, or less, can be cracked in a continuous operation, over long periods of time, without a loss in catalyst activity. Accordingly, the cracking charge stocks should contain less than about 0.1 percent nitrogen, by weight, when continuous operation is desired. Preferably, the nitrogen content should be less than about 0.08 percent, by weight.

In cases in which continuous operation is contemplated and the cracking charge stocks contain more than 0.1 weight percent nitrogen, the nitrogen content should be reduced to an amount less than about 0.1 weight percent, and, preferably, below about 0.08 weight percent, before charging to the process. The reduction in nitro-

gen 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 catalysts such as molybdenum or tungsten oxide, nickel sulfide, tungsten sulfide, cobalt molybdate, cobalt tungstate, etc. As indicated hereinbefore, somewhat higher nitrogen contents can be tolerated, if the operation is intermittent or of relatively short duration. 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 involve 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 be used wherein the catalyst is carried into the reactor in suspension in the hydrocarbon charge or fluidized with the hydrogen and circulated without regeneration. 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.

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.

What is claimed is:

1. A catalytic process for effecting the conversion of a relatively high-boiling 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 C₁-, C₂-, and C₃-gaseous hydrocarbons is less than about 10 percent, by weight, of said relatively high-boiling petroleum hydrocarbon fraction at conversions in which said relatively high-boiling hydrocarbon fraction is completely converted, in a once-through operation, into products boiling below about 410° F.; which comprises contacting said relatively high-boiling hydrocarbon fraction with a catalyst that includes between about 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 selected from the group consisting of a composite of alumina with aluminum halide containing at least about 3 percent aluminum halide, by weight, and a composite of silica with aluminum halide containing at least about 3 percent aluminum halide, by weight, and having an activity index of at least about 30; in the presence of hydrogen; at a temperature varying between about 400° F. and about 850° F.; at a hydrogen pressure varying between about 100 pounds per square inch gauge and about 2500 pounds per square inch gauge; at a liquid hourly space velocity varying between about 0.1 and about 10; and at molar ratios of hydrogen to hydrocarbon varying between about 2 and about 80; and correlating said temperature with said liquid hourly space velocity to produce less than about 10 percent C₁-, C₂-, and C₃-gaseous hydrocarbons, when operating at conversions in which said relatively high boiling hydrocarbon fraction is completely converted in a once-through operation into products boiling below

about 410° F., 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 effecting the conversion of 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 C₁-, C₂-, and C₃-gaseous hydrocarbons is less than about 10 percent, by weight, of said gas oil at conversions in which said gas oil is completely converted in a once-through operation into products boiling below about 410° F.; 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 alumina with aluminum fluoride containing at least about 3 percent aluminum fluoride, by weight, and having an activity index of at least about 30; in the presence of hydrogen; at a temperature varying between about 650° F. and about 850° F.; at a hydrogen pressure varying between about 350 pounds per square inch gauge and about 2000 pounds per square inch gauge; at a liquid hourly space velocity varying between about 0.1 and about 4; and at molar ratios of hydrogen to hydrocarbon varying between about 5 and about 50; and correlating said temperature with said liquid hourly space velocity to produce less than about 10 percent C₁-, C₂-, and C₃-gaseous hydrocarbons, when operating at conversions in which said gas oil is completely converted in a once-through operation into products boiling below about 410° F., 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 effecting the conversion of a relatively high-boiling 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 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 C₁-, C₂-, and C₃-gaseous hydrocarbons is less than about 10 percent, by weight, of said relatively high-boiling petroleum hydrocarbon fraction at conversions in which said relatively high-boiling hydrocarbon fraction is completely converted into products boiling below about 410° F.; which comprises contacting said relatively high-boiling hydrocarbon fraction with a catalyst that includes between about 0.1 percent and about 5 percent, by weight, of platinum deposited upon a synthetic composite of alumina with an aluminum halide containing at least about 3 percent aluminum halide, by weight, and having an activity index of at least about 30; in the presence of hydrogen; at a temperature varying between about 400° F. and about 850° F.; at a hydrogen pressure varying between about 100 pounds per square inch gauge and about 2500 pounds per square inch gauge; at a liquid hourly space velocity varying between about 0.1 and about 10; and at molar ratios of hydrogen to hydrocarbon varying between about 2 and about 80; and correlating said temperature with said liquid hourly space velocity to produce less than about 10 percent C₁-, C₂-, and C₃-gaseous hydrocarbons, when operating at conversions in which said hydrocarbon fraction is completely converted in a once-through operation into products boiling below about 410° F., 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.

References Cited in the file of this patent

UNITED STATES PATENTS

2,479,110	Haensel	Aug. 16, 1949
2,501,197	Veltman et al.	Mar. 21, 1950
2,692,224	Heinemann	Oct. 19, 1954
2,708,180	Fuener et al.	May 10, 1955
2,746,437	Hunter et al.	May 22, 1956
2,763,623	Haensel	Sept. 18, 1956