

July 19, 1960

F. G. CIAPETTA ET AL

2,945,801

CATALYTIC CRACKING

Filed Aug. 11, 1959

2 Sheets-Sheet 1

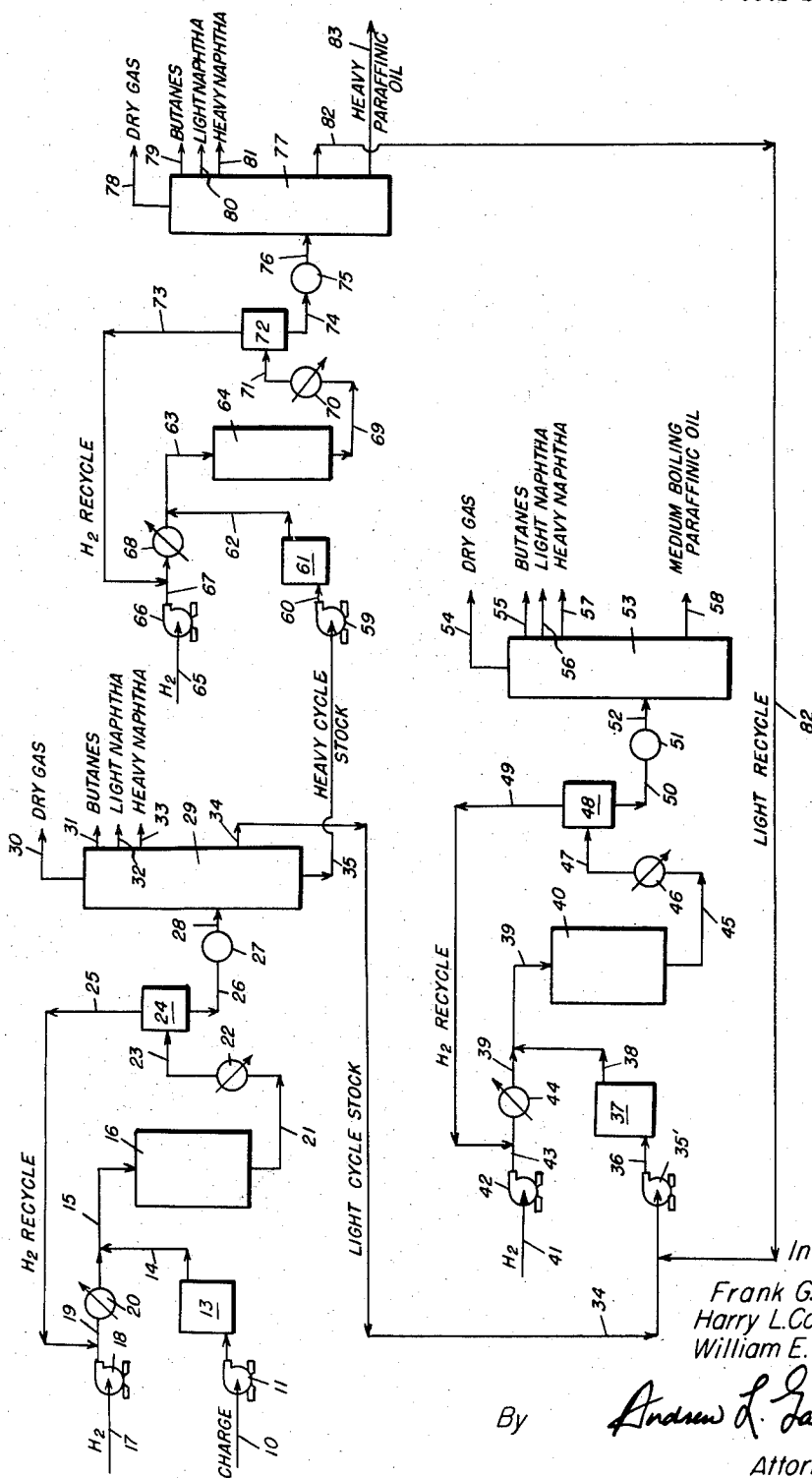


FIG. 1

Inventors
Frank G. Ciapetta
Harry L. Coonradt
William E. Garwood

By *Andrew L. Gaboniantt*
Attorney

July 19, 1960

F. G. CIAPETTA ET AL

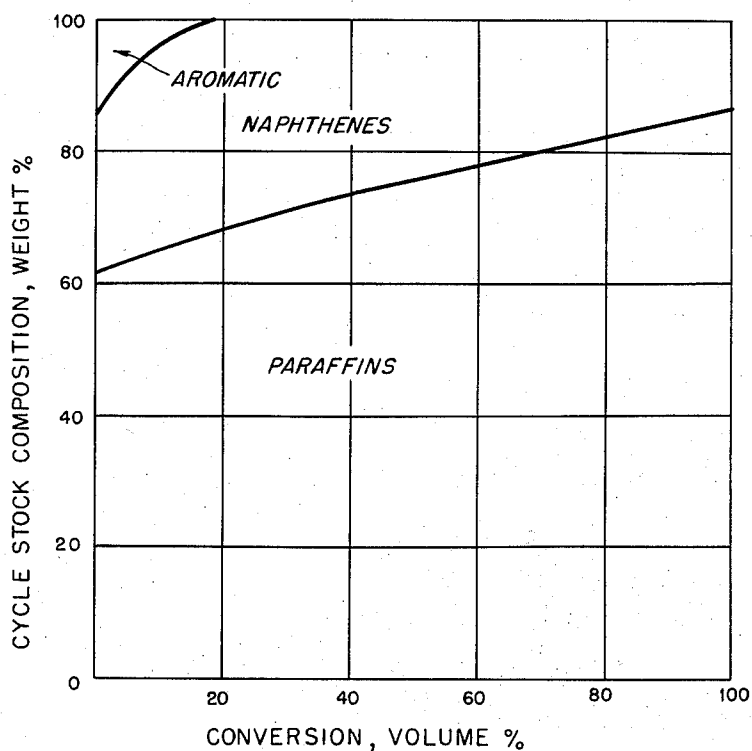
2,945,801

CATALYTIC CRACKING

Filed Aug. 11, 1959

2 Sheets-Sheet 2

FIG. 2



Inventors

Frank G. Ciapetta

Harry L. Coonradt

William E. Garwood

By

Andrew L. Gebmault
Attorney

1

2,945,801

CATALYTIC CRACKING

Frank G. Ciapetta, Silver Spring, Md., and Harry L. Coonradt, Woodbury, and William E. Garwood, Hadonfield, N.J., assignors to Socony Mobil Oil Company, Inc., a corporation of New York

Filed Aug. 11, 1959, Ser. No. 832,950

3 Claims. (Cl. 208—59)

This application is a continuation-in-part of application Serial Number 551,609, filed December 7, 1955, now abandoned.

This invention relates to the catalytic cracking of petroleum hydrocarbon stocks. It is more particularly concerned with a process wherein relatively high boiling hydrocarbon fractions are converted in the presence of platinum- or palladium-containing catalysts into valuable products. As is well known to those familiar with the art, the major products of a cracking operation are dry gas, butanes, light naphtha, heavy naphtha and products boiling at temperatures higher than about 390° F. The heavy naphtha fraction that is obtained by cracking in the presence of hydrogen is a relatively low octane number. Accordingly, in order to produce the high octane gasolines, it is necessary to subject it to a reforming operation. In copending application Serial Number 513,972, filed June 8, 1955, there was disclosed a process for cracking hydrocarbon fractions in a plurality of stages in the presence of hydrogen and of catalysts comprising platinum and palladium series metals deposited upon an acidic oxide carrier. This process has certain advantages over a process wherein hydrocarbons are cracked in a once-through operation. Thus, there is produced less dry gas, less light naphtha, more heavy naphtha and a cycle stock having a higher Diesel Index. In that process, however, the entire cycle stock boiling at temperatures higher than about 390° F. was subjected to cracking in the subsequent stage of the process.

It has now been found that the aforescribed multiple pass process can be operated in an improved manner. It has been discovered that by controlling the amount of cracking in each stage and by cracking portions of the cycle stock in separate reactors, a variety of desirable products can be produced and losses to dry gas and the like can be reduced.

Accordingly, it is an object of this invention to provide a method for producing a variety of valuable products in a cracking operation. Another object is to provide a process for cracking relatively high boiling hydrocarbon fractions that will produce large amounts of valuable products and smaller amounts of less valuable light hydrocarbons and gases. A further object is to provide a process for producing high octane gasoline in increased amounts. A specific object is to provide a process for cracking hydrocarbon charge stocks, in the presence of hydrogen, and of catalysts comprising metals of the platinum and palladium series deposited upon a synthetic composite of two or more refractory oxides which has a relatively high cracking activity, that will produce the aforementioned results. Another specific object is to provide a process for cracking a hydrocarbon charge stock, in the presence of hydrogen and of catalysts containing platinum and palladium series metals, that will produce increased amounts of high octane gasoline and other valuable hydrocarbon products.

Other objects and advantages of this invention will become apparent to those skilled in the art from the

2

following detailed description considered in conjunction with the drawings in which:

Figure 1 presents a schematic arrangement of an embodiment of the process of this invention; and

Figure 2 shows the graphic relationship between the volume percent conversion into products boiling below about 390° F. and the hydrocarbon distribution of the product boiling at temperatures higher than about 390° F. obtained by cracking a typical gas oil in the presence of hydrogen and of a platinum-containing catalyst.

Stated broadly, the present invention provides a process for producing valuable hydrocarbon products which comprises contacting, in a first reaction zone, 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, 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 at least two refractory oxides, said composite having an activity index of at least about 25, in the presence of hydrogen in amounts, expressed in molar ratio of hydrogen to hydrocarbon charge, within the range about 2 to about 80, at a pressure above about 100 pounds per square inch gauge, at a liquid hourly space velocity within the range about 0.1 to about 10, and at a temperature above about 400° F. to effect conversions into products boiling at temperatures lower than about 390° F. within the range about 5 volume percent to about 50 volume percent, and to produce an effluent material comprising products boiling at temperatures lower than about 390° F., a product boiling at temperatures higher than about 390° F. and a gaseous fraction rich in hydrogen; separating said product boiling at temperatures higher than about 390° F. into a lower boiling fraction and a higher boiling fraction, said lower boiling fraction having a boiling range varying between about 390° F. and about 450–750° F. and said higher boiling fraction having a boiling range varying between about 450–750° F. and the end boiling point of said product boiling at temperatures higher than about 390° F., contacting each of said fractions in a separate reaction zone with a catalyst of the type used in the first reaction zone, in the presence of hydrogen in amounts, expressed in molar ratio of hydrogen to hydrocarbon charge within the range about 2 to about 80, at a pressure above about 100 pounds per square inch gauge, at a liquid hourly space velocity within the range about 0.1 to about 10, and at a temperature above about 400° F. to produce from said lower boiling fraction a naphthenic naphtha and a medium boiling range paraffinic stock, and to produce from said higher boiling fraction naphthenic naphtha and a high boiling range paraffinic stock.

Throughout the specification and the claims, the term "conversion" is intended to be a generic term for the amount of products boiling at temperatures lower than about 390° F. (100-recycle), of gasoline, of fuel oil, or of cycle stock obtained in the process. It is expressed in terms of the volume percent of the initial charge which is transformed in the process. The amount of product boiling at temperatures lower than about 390° F. is obtained by subtracting the volume percent of cycle stock (fuel oil) that boils at temperatures higher than about 390° F. from 100 percent, i.e., from the initial volume of the charge. The expression "(100-recycle)" is an abbreviation for 100 percent minus the volume percent recycle. As the cycle stock (i.e., the effluent boiling at temperatures higher than about 390° F.) is an excellent fuel oil, conversion into fuel oil is the volume percent of product which boils at temperatures higher than about

390° F. The volume percent of conversion into products boiling at temperatures lower than about 390° F. (100-recycle) and the volume percent of conversion into fuel oil totals to 100 volume percent, based upon the initial charge. "Dry gas" refers to the methane, ethane, propane, and ethylene and propylene produced in a cracking process, expressed in terms of weight percent of the initial charge. "C₅+ light naphtha" is the product that boils between about 80° F. and about 170° F. The "heavy naphtha" is the product that boils between about 170° F. and about 390° F. The "diesel index" of the fuel oil is a function of the A.P.I. gravity and of the aniline number, as defined by Becker et al. in the S.A.E. Journal (Transactions), vol. 35, No. 4, p. 377. 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 conditions, in the "Cat. A" test. This test is described by Alexander and Shimp in National Petroleum News, 36, page R-537 (August 2, 1944). The unit for rating the cracking activity of a material is called the "activity index" (A.I.).

The catalysts utilizable herein are those described in copending application Serial Number 351,151, filed on April 27, 1953, now abandoned; and in the continuation-in-part thereof, Serial Number 825,016, filed on July 6, 1959. Briefly, these catalysts comprise between about 0.05 percent, by weight, and about 20 percent, by weight of the final catalyst, preferably between about 0.1 percent and about 5 percent, by weight, of the metals of the platinum and palladium series, i.e., those having Atomic Numbers of 44-46, inclusive, 76-78, inclusive, supported upon synthetic composites of two or more refractory oxides. The carrier is a synthetic composite of two or more oxides of the metals of groups IIA, IIIB and IVA and B of the Periodic Arrangement of Elements [J. Chem. ed., 16, 409 (1939)]. These synthetic composites of refractory oxides must have an activity index of at least about 25. They can also contain halogens and other materials which are known in the art as promoters for cracking catalysts, or small amounts of alkali metals that are added for the purpose of controlling the activity index of the carrier. Non-limiting examples of the composites contemplated herein include silica-alumina, silica-zirconia, silica-alumina-zirconia, alumina-boria, silica-alumina-fluorine, and the like. The preferred support is a synthetic composite of silica and alumina containing between about 1 percent, by weight, and about 90 percent, by weight, of alumina. These synthetic composites of two or more refractory oxides can be made of the usual methods known to those skilled in the art of catalyst manufacture. Examples of methods of preparing them are set forth in copending applications Serial Numbers 351,151, now abandoned, and 825,016, referred to hereinafter.

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

EXAMPLE 1

A synthetic silica-alumina carrier or support containing 10 percent, by weight, alumina was prepared by mixing an aqueous solution of sodium silicate (containing 158 g. per liter of silica) with an equal amount of an aqueous acid solution of aluminum sulfate containing 39.4 g. Al₂(SO₄)₃ and 28.6 g. concentrated H₂SO₄ per liter. The mixture was dropped through a column of oil wherein gelation of the hydrogel was effected in bead form. The bead hydrogel was soaked in hot water (about 120° F.) for about 3 hours. The sodium in the hydrogel was then removed by exchanging the gel with an aqueous solution of aluminum sulfate [1.5% Al₂(SO₄)₃ by weight] containing a small amount (0.2 percent by weight) of ammonium sulfate. The thus-exchanged hydrogel bead was water-washed. Then, it was dried in superheated steam (about 280-340° F.)

for about 3 hours and, finally, calcined at 1300° F. under a low partial pressure of steam for about 10 hours. The silica-alumina beads were then crushed to pass through a 14-mesh screen and the material retained on a 25-mesh screen (U.S. Standard Screen Series) was used for catalyst preparation.

Portions of the crushed, calcined carrier were then barely covered with aqueous solutions of chloroplatinic acid, of concentrations sufficient to produce the desired amount of metal in the finished catalyst. The excess solution was removed by centrifuging. The thus-impregnated carrier was then wet-aged in a lightly covered vessel at 230° F. for 24 hours. The catalyst was treated with hydrogen for four hours at 400° F. Then, it was activated in hydrogen for 16 hours before it was used. The catalyst thus-prepared contained 0.47 percent platinum, by weight of the catalyst, and the silica-alumina carrier had an activity index of 46.

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

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

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

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

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

5

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

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

The 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.

Accordingly, it is preferable that the cracking charge stocks contain less than about 0.1 percent nitrogen, by weight, when continuous operation of long duration is desired. Preferably, the nitrogen content should be less than about 0.08 percent, by weight. 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 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.

A schematic arrangement of a method of operating the process of this invention is set forth in Figure 1. A hydrocarbon charge stock as aforedescribed is introduced through a pipe 10 and pumped by means of a suitable pumping device 11 through a pipe 12 into a furnace or other suitable heating device 13. In the heater 13, the hydrocarbon charge is heated to reaction temperature. The thus heated charge is passed through pipes 14 and 15 into a first stage reactor 16. Hydrogen, or a gas rich in hydrogen, is introduced through a pipe 17 and pumped and compressed to the desired operating pressure by means of a compressor 18. The compressed gas is passed through a pipe 19 and a heater 20, thence through pipe 15 to be commingled with the hydrocarbon charge and passed to the reactor 16.

The reactor 16 contains a fixed bed of a platinum or palladium series metal catalyst of the type described hereinbefore. The reaction conditions of temperature, pressure and space velocity in the reactor 16 are controlled to effect conversions varying between about 5 percent and about 50 percent by volume of products boiling lower

6

than about 390° F. The volume percent conversion will vary dependent upon the charge stock so that the cycle stock will contain a predetermined amount of cyclic hydrocarbons. In no event will the volume percent conversion exceed 50 volume percent. The products are withdrawn from the reactor 16 through a pipe 21 and passed through a heat exchanger 22 or other cooling device, wherein it is cooled to temperatures at which hydrogen gas can be separated. The thus-cooled effluent is then passed through a pipe 23 into a high pressure gas separator 24.

In the gas separator 24, the effluent is separated into a liquid phase and a gas phase that comprises substantially pure hydrogen. This gas is removed from the gas separator through a pipe 25 and recycled through pipe 19 to supply a portion of the hydrogen required in the process. The liquid product from the gas separator 24 is passed through a pipe 26 into a depressuring zone 27 and thence through a pipe 28 into a fractionator 29.

In the fractionator 29, the products are separated into several fractions. The dry gas is removed through a pipe 30 and can be sent to the gas plant or other gas processing units. Butanes are removed through a pipe 31 for use in the blending of finished gasolines. The C_5+ light naphtha is removed through a pipe 32 and is also utilized for gasoline blending. The heavy naphtha fraction is removed through a pipe 33. This naphtha is highly naphthenic and can be reformed to produce excellent yields of high octane gasoline, by means of conventional methods of reforming hydrocarbon fractions in the presence of hydrogen and of suitable catalysts. A lower-boiling fraction of the product boiling at temperatures higher than about 390° F., i.e., light cycle stock, is removed through a pipe 34. The end boiling point of this light cycle stock will vary between about 450° F. and about 750° F. Generally the cut point, i.e., the end boiling point of this fraction is controlled so that the light cycle stock will contain a greater relative amount of cyclic hydrocarbons than the original charge. The light cycle stock is passed to a second reactor as described hereinafter.

A higher boiling fraction of the products boiling at temperatures above about 390° F., i.e., heavy cycle stock, is removed through pipe 35. This fraction will boil between the end boiling point of the light cycle stock and the end boiling point of the products boiling at temperatures higher than about 390° F. The heavy cycle stock is predominately paraffinic.

As was mentioned hereinbefore, the light cycle stock is subjected to further cracking. It is passed through pipe 34 into a pump 35' and thence through a pipe 36 into a furnace, or other heating device, 37. In the furnace 37, the cycle stock is heated to the desired temperature. The thus-heated light cycle stock is passed through pipes 38 and 39 into a separate, second reactor 40. Hydrogen is introduced through a pipe 41 and compressed in a compressor 42 to the desired reaction pressure. The compressed hydrogen is passed through a pipe 43, heated in a heater 44, and then passed into the reactor 40 through pipe 39 in admixture with the heated light cycle stock.

In the reactor 40 the mixture of hydrogen and light cycle stock is contacted with a platinum or palladium series metal catalyst of the type described hereinbefore to effect further cracking of the charge. The catalyst contained in the reactor 40 can be of the same type as that contained in reactor 16, or it can be a different platinum or palladium series metal catalyst. The reaction conditions in the reactor 40 will be controlled so that the amount of conversion into products boiling at temperatures below about 390° F. will not exceed 50 volume percent. The total effluent from the reactor 40 is passed through a pipe 45 and through a condenser 46 wherein it is cooled to temperatures at which hydrogen can be separated. The thus-cooled effluent is passed through a pipe 47 into a high pressure gas separator 48.

In the gas separator 48 the effluent is separated into a gaseous phase and a liquid phase. The gaseous phase comprises substantially pure hydrogen gas and it is recycled to the process through a pipe 49 and thence through pipe 43 to supply a portion of the hydrogen required in the process. The liquid fraction obtained in the gas separator 48 is passed through a pipe 50 into a depressuring zone 51, and thence through a pipe 52 into a fractionator 53.

In the fractionator 53, the products are separated into suitable fractions. Dry gas is removed through a pipe 54 and passed to the gas plant. Butanes are removed through a pipe 55 and C_5+ light naphtha is removed through a pipe 56. The butanes and the light naphtha can be used for gasoline blending. Heavy naphtha fraction is removed through pipe 57. This heavy naphtha is highly naphthenic in character and can be reformed to produce excellent yields of high octane gasoline along with the heavy naphtha that has been removed through pipe 33. The material boiling at temperatures higher than about 390° F. is removed through a pipe 58. This material is a medium boiling fraction that boils within the boiling range of heavy jet fuels and No. 2 fuel oil. The material is highly paraffinic. Accordingly, it can be used to produce fuel oils or jet fuels that have a very high heat content. This material also has a very high diesel index and is, therefore, very useful as a diesel fuel. Because of the paraffinic nature of the medium boiling fraction, it will have a high smoke point, which property, together with the high heat content, renders it valuable as a jet fuel.

The heavy cycle stock that is removed through pipe 35 is pumped by means of a pump 59 through a pipe 60 into a furnace, or other heating device, 61. In the furnace 61, the heavy cycle stock is heated to the desired reaction temperature. The thus-heated material is passed through pipes 62 and 63 into a third reactor 64. Hydrogen gas is introduced through a pipe 65 and is compressed to reaction pressure by means of a compressor 66 and passed through a pipe 67 into a heater 68. The hydrogen is heated to a suitable temperature in heater 68 and then passed through pipe 63 where it is admixed with the hydrocarbon charge. The mixture of hydrogen and charge is passed into the reactor 64.

In the reactor 64, the mixture of hydrogen and hydrocarbon charge is contacted with a platinum or palladium series metal catalyst of the type described hereinbefore, to effect further cracking of the heavy cycle stock. The catalyst contained in reactor 64 can be the same as that contained in reactors 16 or 40 or it can be a different type of platinum or palladium series metal catalyst. The reaction conditions maintained in the reactor 64 are controlled to effect a conversion into products boiling lower than about 390° F. of no greater than about 25 volume percent. The total effluent from the reactor 64 is passed through a pipe 69 and through a condenser 70, wherein it is cooled to temperatures at which hydrogen can be separated. The thus-cooled effluent is passed through a pipe 71 into a high pressure gas separator 72.

In the gas separator 72, the effluent is separated into a gaseous phase and a liquid phase. The gaseous phase, comprising substantially pure hydrogen, is recycled to the process through a pipe 73 and thence through pipe 67 to supply a portion of the hydrogen required in the process. The liquid product obtained in the gas separator 72 is passed through a pipe 74 into a depressuring zone 75 and thence through a pipe 76 into a fractionator 77.

In the fractionator 77, the products are separated into suitable fractions. Dry gas is removed through a pipe 78 and passed to gas processing. Butanes are removed through a pipe 79 and light naphtha is removed through a pipe 80. The butanes and light naphtha can be used for gasoline blending. A heavy naphtha fraction is removed through a pipe 81. This naphtha is also of a highly

naphthenic character. Accordingly, it can be reformed to produce excellent yields of high octane gasoline. A medium boiling fraction boiling between about 390° F. and about 450–750° F. is removed through a pipe 82. The end boiling point is selected so that the medium boiling fraction has a greater proportion of cyclic hydrocarbons than the initial charge. This material can be cycled to be processed in reactor 40 together with the light cycle stock introduced through pipe 34. The higher boiling fraction in the fractionator 77 is removed through a pipe 83. This material has an initial boiling point varying between about 450° F. and about 750° F. and an end boiling point varying between about 500° F. and about 900° F. It is highly paraffinic. Accordingly, this high boiling fraction, after suitable finishing operations, is utilizable as white oil, or as lubricating oils that have a high viscosity index.

In order to produce the valuable products obtained in the present process, it is necessary to control the amount of conversion in each reactor within defined limits. This is done by suitable control of the reaction conditions of temperature, pressure and space velocity in the reactor. The proper set of reaction conditions to effect a desired amount of conversion into products boiling below about 390° F. for any given charge stock can be readily determined by those skilled in the art. The method of determining the proper set of conditions is fully illustrated and described in copending application Serial No. 418,166, filed on March 23, 1954, now abandoned and reference should be made thereto.

It is particularly important that the amount of conversion into products boiling below about 390° F. be rigidly controlled in the first reactor. This will become apparent from the following example:

EXAMPLE 2

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

A.P.I. gravity.....	36.7
A.S.T.M. distillation:	
I.B.P.....	° F... 436
50%.....	° F... 524
E.B.P.....	° F... 666
Sulfur, weight percent.....	0.2
Aromatics, weight percent.....	15
Naphthenes, weight percent.....	23
Paraffins, weight percent.....	62

In a series of runs, the light East Texas gas oil was subjected to cracking in the presence of hydrogen and of the catalyst described in Example 1, after the latter had reached equilibrium, i.e., had been in continuous operation for more than 5 days. The hydrogen pressure used was 1000 p.s.i.g., the liquid hourly space velocity was 0.5, and the molar ratio of hydrogen-to-oil was 40. Each run was carried out under these conditions but at a different temperature. The product distribution for each run was noted. The pertinent data are set forth in Table I.

Table I

	640	685	700
Temperature, ° F.....	13.3	44.1	68.2
Conversion, Vol. Percent ¹	0.4	1.9	2.1
Dry Gas, Wt. Percent.....	1.3	4.7	8.5
Butanes, Vol. Percent.....	2.4	10.1	17.2
C_5+ Lt. Naphtha, Vol. Percent.....	15.2	37.4	56.4
Heavy Naphtha, Vol. Percent.....	86.7	55.9	31.8
Cycle Stock, Vol. Percent.....			
Aromatics, Wt. Percent.....	2	nil	nil
Naphthenes, Wt. Percent.....	35	25	20
Paraffins, Wt. Percent.....	63	75	80

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

Fig. 2 is based upon the data set forth in Table I. Fig. 2 shows the relationship between the volume percent conversion into products boiling at temperatures lower

than about 390° F. and the weight percent hydrocarbon distribution of the cycle stock obtained by cracking the light East Texas gas oil at different conversion levels. It will be noted that the amount of paraffins in the cycle stock steadily increases as the amount of conversion is increased. Concurrently, the amount of naphthenes diminishes. The aromatic hydrocarbons no longer appear in the products at conversion levels of greater than about 20 volumes percent.

It is a feature of this invention that the cycle stock obtained in the first reaction stage must have a relatively high cyclic content. Accordingly, the amount of conversion into products boiling at temperatures lower than about 390° F. should be no greater than 50 percent. In general, the cyclic hydrocarbons are in the lower boiling portion of the cycle stock. Thus when the cycle stock is fractionated, as aforesaid, to produce a lower boiling fraction of high cyclic content, this fraction contains the bulk of the cyclic content of the cycle stock. Accordingly, at conversion levels greater than about 50 percent the relative amount of low-boiling cycle stock fraction will be too small for practical application of the process of this invention. In general, therefore, the amount of conversion, in the first stage reactor, into products boiling at temperatures lower than about 390° F. should be between about 5 volume percent about 50 volume percent. The particular degree of conversion within this range will, of course, vary with different charge stocks.

It will be noted that, throughout the specification and claims, about 390° F. has been used as the measure of the amount of cracking. This has been used, because reformer naphtha charge stocks usually are selected to have an end boiling point of about 390° F. In many applications, however, the end boiling point selected for the naphtha can be lower or higher, e.g., 360° F. or 410° F. In such a case, the measure of cracking will be that of the naphtha, 360° F. or 410° F. The other considerations and manipulations in the process of this invention will be the same as aforesaid described.

The process of this invention is usually carried out at temperatures above about 400° F. and generally within the range about 500° F. to about 825° F. and preferably within the range 650° F. to about 825° F. The liquid hourly space velocity should be within the range about 0.1 to about 10, preferably, between about 0.1 and 4. The hydrogen pressure employed will usually be above 100 pounds per square inch gauge and generally within the range about 100 pounds per square inch gauge (p.s.i.g.) to about 2500 pounds per square inch gauge. Preferably, the pressure should be within the range about 350 to about 2000 pounds per square inch gauge. The molar ratio of hydrogen to hydrocarbon will be within the range about 2 and about 80, preferably, between about 5 and about 50.

The process of this invention can be carried out using conventional apparatus and schemes for effecting recycle operation in catalytic cracking. As the catalyst remains active over long periods of time before it must be regenerated, the operation is advantageously carried out using a fixed bed of catalyst. Other techniques, however, can be used, such as, the moving bed technique or the fluid technique.

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

What is claimed is:

1. A process for producing valuable hydrocarbon products which comprises contacting in a first reaction zone, 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, with a catalyst comprising between about 0.05 percent and about 20 percent, by weight of the catalyst, 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 of at least two solid refractory oxides of elements of groups IIA, IIIB and IV of the periodic arrangement of the elements, said composite having an activity index of at least 25, in the presence of hydrogen in amounts, expressed in molar ratio of hydrogen to hydrocarbon charge, within the range about 2 to about 80, at a pressure 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 a temperature within the range about 500° F. to about 825° F., to effect conversion into products boiling at temperatures lower than about 390° F. within the range about 5 volume percent and about 50 volume percent and to produce an effluent material comprising products boiling at temperatures lower than about 390° F., a product boiling at temperatures higher than about 390° F. and a gaseous fraction rich in hydrogen; separating said product boiling at temperatures higher than about 390° F. into a lower boiling fraction and a higher boiling fraction, said lower boiling fraction having a boiling range within the range about 390° F. to about 450°-750° F. and said higher boiling fraction having a boiling range within the range about 450°-750° F. to the end boiling point of said product boiling at temperatures higher than about 390° F., contacting each of said fractions in a separate reaction zone with a catalyst of the type used in said first reaction zone, in the presence of hydrogen in amounts, expressed in molar ratio of hydrogen to hydrocarbon charge, within the range about 2 to about 80, at a pressure 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 a temperature within the range about 400° F. to about 825° F. to produce from said lower boiling fraction, a naphthenic naphtha and a medium boiling range paraffinic stock and to produce from said higher boiling fraction a naphthenic naphtha and a high boiling range paraffinic stock.

2. A process for producing valuable hydrocarbon products which comprises contacting, in a first reaction zone, 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 with a catalyst comprising between about 0.1 percent and about 5 percent, by weight of the catalyst, of platinum deposited upon a synthetic composite of silica and alumina, said composite having an activity index of at least 25, in the presence of hydrogen in amounts, expressed in molar ratio of hydrogen to hydrocarbon charge, within the range about 5 to about 50, at a pressure 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 a temperature within the range about 650° F. to about 825° F. to effect conversion into products boiling at temperatures lower than about 390° F. within the range about 5 volume percent to about 50 volume percent, and to produce an effluent material comprising products boiling at temperatures lower than about 390° F., a product boiling at temperatures higher than about 390° F. and a gaseous fraction rich in hydrogen; separating said product boiling at temperatures higher than about 390° F. into a lower boiling fraction and a higher boiling fraction, said lower boiling fraction having a boiling range within the range about 390° F. to about 450°-750° F.

11

and said higher boiling fraction having a boiling range within the range about 450°-750° F. and the end boiling point of said product boiling at temperatures higher than about 390° F., contacting each of said fractions in a separate reaction zone with a catalyst of the type used in said first reaction zone, in the presence of hydrogen in amounts, expressed in molar ratio of hydrogen to hydrocarbon charge, within the range about 5 to about 50, at a pressure 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 a temperature within the range about 650° F. to about 825° F. to produce from said lower boiling fraction, a naphthenic naphtha and a medium boiling range paraffinic stock, and to produce from said higher boiling fraction a naphthenic naphtha and a high boiling range paraffinic stock.

3. A process for producing valuable hydrocarbon products which comprises: contacting, in a first reaction zone, 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. with a catalyst comprising between about 0.05 percent and about 20 percent, by weight of the catalyst, 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 of at least two solid refractory oxides of elements of groups IIA, IIIB and IV of the periodic arrangement of the elements, said composite having an activity index of at least 25, in the presence of hydrogen in amounts, ex-

12

pressed in molar ratio of hydrogen to hydrocarbon charge within the range about 2 to about 80, at a pressure above about 100 pounds per square inch gauge, at a liquid hourly space velocity within the range about 0.1 to about 10 and at a temperature above about 400° F. to effect conversion into products boiling at temperatures below about 390° F. in an amount within the range about 5 to 50 volume percent of the initial charge and produce an effluent comprising products boiling below 390° F., a product boiling above 390° F. and a gaseous fraction rich in hydrogen; separating said product boiling above about 390° F. into a lower boiling fraction boiling within the range about 390° F. to 450°-750° F., and a higher boiling fraction, boiling within the range about 450°-750° F. to the end point of said product boiling at temperatures above 390° F.; contacting each of said fractions in a separate reaction zone with a catalyst of the type used in said first reaction zone, in the presence of hydrogen in amounts, expressed in molar ratio of hydrogen to hydrocarbon charge, within the range about 2 to about 80, at a hydrogen pressure above about 100 pounds per square inch gauge, at a liquid hourly space velocity within the range about 0.1 to about 10, and at a temperature above about 400° F., to produce from said lower boiling fraction a naphthenic naphtha and a medium boiling range paraffinic stock and to produce from said higher boiling fraction a naphthenic naphtha and a higher boiling range paraffinic stock.

No references cited.