

1

2,945,802

PRODUCTION OF HIGH QUALITY LIGHT JET FUEL

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This invention is directed to fuels utilizable in jet combustion devices. It is more particularly concerned with an improved process whereby there are produced high quality jet fuels and aromatic hydrocarbons.

As is well known to those familiar with the art, the term "jet combustion" refers to a method of combustion wherein fuel is continuously introduced into and continuously burned in a confined space, for the purpose of deriving power directly from the hot products of combustion. The most complicated forms of jet engines presently proposed consist of a propulsion or jet tube, closed at one end, plus a gas turbine which extracts sufficient energy from the departing gases to drive the compressor. In present commercial forms, the compressor and turbine are assembled axially upon a common shaft, spaced far enough apart to permit a number of combustion chambers to be arranged about the shaft between the compressor and turbine, with an exhaust tube extending rearwardly from the turbine. The principal application of such engines is in powering aircraft, particularly for high-altitude operations. Therefore, the desiderata of fuels utilizable in jet combustion devices are many and varied.

As is well known to those familiar to the art, aromatic hydrocarbons such as benzene and alkyl benzenes are highly desirable as solvents and as raw materials for numerous well known chemical processes. It is a feature of the present invention to provide valuable aromatic hydrocarbon fractions together with jet fuels of superior characteristics.

Present commercial processes for preparing monocyclic aromatics from petroleum naphthas, involving reforming over various catalysts followed by extraction of aromatics with various solvents, all have several problems in common. Naphthas having low sulfur and low olefin content must be used or a pretreating step is necessary before reforming. A more serious problem is disposal of the raffinate from the extraction step; its low octane number makes it undesirable as motor fuel, and it is a poor recycle charge stock to the reformer. Additional processing of the raffinate, such as thermal cracking and catalytic cracking, have been suggested to improve the over-all yield of monocyclic aromatics, but poor selectivity makes such processing wasteful.

It has now been found that the properties of jet fuels produced by hydrocracking a high boiling charge stock in the presence of the cracking catalyst, preferably a platinum or palladium series metal catalyst, can be markedly improved by a method that is simple and economical and which simultaneously provides substantial quantities of valuable aromatic hydrocarbons. It has been discovered that when the portion of a lower boiling range jet fuel, obtained by hydrocracking, that boils in the naphtha boiling range is replaced by the paraffinic raffinate produced by extracting the reformate obtained by reforming this naphtha portion, the properties of the jet fuel are greatly improved. It is also a feature of this invention that the aromatic extract of the reformate pro-

2

vides substantial quantities of valuable aromatic hydrocarbons.

Accordingly, it is an object of this invention to provide an improved jet combustion fuel. Another object is to provide a simple process for producing an improved lower boiling range jet fuel and valuable aromatic hydrocarbons. A further object is to provide a jet fuel of improved properties that is obtained by cracking in the presence of hydrogen and of a suitable hydrocracking catalyst. A specific object is to provide a jet fuel having improved properties that is obtained by cracking in the presence of a catalyst that contains a metal of the platinum or palladium series. Another specific object is to provide a method for producing improved jet combustion fuels and valuable aromatic hydrocarbons that involves cracking higher boiling charge stocks in the presence of hydrogen and of a hydrocracking catalyst, replacing the portion of the hydrocracked jet fuel boiling in the naphtha boiling range with a paraffinic extract obtained from a reformate produced by reforming the naphtha portion, and separating from the extract of said reformate a valuable aromatic hydrocarbon. A further specific object is to provide jet combustion fuels that are produced by such process.

Other objects and advantages of the present invention will become apparent to those skilled in the art from the following detailed description considered in conjunction with the drawing which shows a schematic arrangement of a typical embodiment for carrying out a process of this invention.

In general, the present invention provides a method for producing a jet combustion fuel and aromatic hydrocarbons that comprises contacting a hydrocarbon charge stock with a hydrocracking catalyst in the presence of hydrogen in amounts, expressed in molar ratio of hydrogen to hydrocarbon charge, varying between about 2 and about 80, under hydrocracking conditions, to convert at least a portion of the hydrocarbon charge into a jet fuel having an initial boiling point of about 160° F. and an end-boiling point of about 450–550° F.; separating said jet fuel into a cracked naphtha fraction and a fraction having an initial boiling point of about 300–400° F. and an end-boiling point of about 450–550° F.; separately reforming said cracked naphtha fraction in the presence of a reforming catalyst and under reforming conditions; separating the reformate into a paraffinic fraction and an aromatic fraction; combining said paraffinic fraction with said fraction having an initial boiling point of about 300–400° F. and an end-boiling point of about 450–550° F. to produce a jet fuel; and recovering aromatic hydrocarbons from said aromatic fraction.

Throughout the specification and the claims, "dry gas" refers to the methane, ethane, propane, and ethylene and propylene produced in a cracking process, expressed in terms of weight percent of the initial charge. "Light naphtha" boils in the range varying between about 80° F. and about 160–225° F. The "heavy naphtha" fraction boils in the range varying between about 160–225° F. (initial boiling point) and about 300–400° F. (end-boiling point). The "aniline-gravity product" is expressed as the product of the A.P.I. gravity and the aniline number, as described in ASTM Test Methods D611 and D287. The "smoke point" is obtained by Method 2107 of Federal Specification VV-L-791. The cracking activity of a carrier for the cracking catalyst used herein 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 such a carrier is called the "activity index" (A.I.).

The process of this invention will be understood from

the figure, which sets forth a schematic arrangement of a method for carrying out the process of the present invention. A suitable hydrocarbon charge stock is introduced through a pipe 10 and pumped by means of a suitable pumping device 11 through a pipe 12 into a heater 13. In the heater 13 the charge stock is heated to reaction temperature. The thus-heated charge then is passed through pipes 14 and 15 into a reactor 16.

Hydrogen gas, or a gas rich in hydrogen, is introduced through a pipe 17 and pumped and compressed by means of a compressor 18. The compressed hydrogen passes through a pipe 19 into a heat exchanger or heating device 20 wherein it is heated to reaction temperature. The thus-heated hydrogen is then commingled with the hydrocarbon charge in pipe 15 and the mixture then passes into the reactor 16. The reactor 16 can be a single reactor or comprise a plurality of reaction beds.

In the reactor 16 there is contained a bed or plurality of beds of a suitable hydrocracking catalyst, such as molybdenum oxide or platinum-containing catalyst, as described hereinafter. The mixture of hydrogen and hydrocarbon charge is contacted with the catalyst in the reactor 16 under suitable conditions to effect at least partial conversion of the hydrocarbon charge into a lower boiling range jet fuel. It is understood, of course, that the degree of conversion used will depend upon the amount of jet fuel desired in a specific operation. In an extreme case, the entire charge material can be converted into jet fuel. The total effluent from the reactor 16 is removed through a pipe 21 and passed into a heat exchanger or suitable cooling device 22. In the heat exchanger 22, the effluent is cooled to temperatures at which gaseous hydrogen can be separated from liquid phase. The thus-cooled effluent is passed through a pipe 23 into a high pressure separator 24.

In the high pressure separator 24 there are a liquid phase and a gaseous phase. The gaseous phase, containing substantial amounts of hydrogen, is removed through a pipe 25 and can be recycled to the process through pipe 19. The liquid product from the high pressure separator 24 is removed through a pipe 26, passed through a depressuring zone 27 and thence through a pipe 28 into a suitable fractionating device 29.

In the fractionator 29, the liquid products are separated into suitable fractions. Dry gas is removed through a pipe 30 and can be sent to the gas processing plant. The butanes are removed through a pipe 31 and the light naphtha is removed through a pipe 32. Heavy naphtha is removed through a pipe 33. The materials removed via pipes 31 and 32 can be utilized for gasoline blending or as chemical raw materials. A fraction boiling at temperatures within the range varying between about 300-400° F. (initial boiling point) and about 450-550° F. (end-boiling point) is removed through a pipe 34. The material boiling at temperatures higher than about 450-550° F. is removed through a pipe 35. If desired, this material can be recycled to the process via pipe 12.

The heavy naphtha removed through pipe 33 is subjected to reforming. It is passed through pipe 33 into a pumping device 41 and thence through a pipe 42 into a suitable heater 43. In the heater 43, the naphtha is heated to suitable reforming temperature. The thus-heated naphtha is passed through a pipe 44 and a pipe 45 into a reforming unit 46. Hydrogen gas is introduced through a pipe 47 into a suitable pumping and compressing device 48. The compressed hydrogen then passes through a pipe 49 into a heat exchanger or heating device 50 wherein it is heated to reaction temperature. The thus-heated hydrogen is then commingled with the hydrocarbon charge in pipe 45 and the mixture passes into the reforming unit 46.

The reforming unit 46 can be any reforming system well known to those skilled in the art. Accordingly, it can comprise one or more fixed catalyst beds which may or may not be provided with intermediate reheaters.

The unit may also comprise a moving bed or a fluidized bed type reactor. In the reactor 46, the naphtha and hydrogen are contacted with a suitable reforming catalyst under reforming conditions. The reformate is withdrawn through pipe 51 and cooled by means of a heat exchanger or cooling device 52 to temperatures at which gaseous hydrogen can be separated from the liquid phase. The thus-cooled effluent is then passes through a pipe 53 into a high pressure separator 54.

In the high pressure separator 54, there are a liquid phase and a gaseous phase. The gaseous phase containing substantial amounts of hydrogen is removed through a pipe 55 and can be recycled to the process to pipe 49. In most reforming processes, there is effected a net production of hydrogen. Accordingly, at least a portion of the hydrogen-rich gas withdrawn through pipe 55 can be cycled to the hydrocracking operation via pipe 55a to provide at least a portion of the hydrogen requirement thereof. The liquid product from the high pressure separator 54 is removed through a pipe 56 and passed through a depressuring zone 57 and thence through a pipe 58 into an extraction device 59. In some cases, it will be desirable to remove dry gas, butanes, and/or pentanes from the reformate before it is subjected to extraction. This can be done in a suitable gas separator (not shown).

In the extraction device 59, the reformate is separated into a raffinate and extract phase by means of a suitable solvent. This is accomplished by introducing a solvent such as glycol or SO₂ into the extractor 59 via a pipe 60. The solvents in contact with the reformate hydrocarbons extract an aromatic fraction that is removed through pipe 61 and passes into a separator 62. In the separator 62, a cut rich in aromatic hydrocarbons is removed through pipe 63 and the solvent is removed through a pipe 64 and can be recycled to pipe 60. The aromatic cut that is removed through pipe 63 can be utilized in a number of ways. It can be used as a raw material for the production of aromatic derivatives, utilizing processes well known to the art. This fraction also has a very high blending octane number. Accordingly, it can be used as blending stock for the production of gasolines with a high performance number.

The raffinate obtained in extractor 59 is predominantly composed of paraffinic hydrocarbons. This raffinate is removed through a pipe 65 and passed into a separator 66 where any trace amounts of solvent that may be present can be removed. The paraffinic raffinate is then passed through a pipe 67 into a blending operation 68. In the blending operation 68 the fraction from the hydrocracking operation that is removed through pipe 34 is blended with the paraffinic raffinate provided through pipe 67, thus producing a high quality light jet fuel that is removed through pipe 69.

The jet fuels that are improved by the process of this invention are produced by cracking a gas oil in the presence of hydrogen and of suitable cracking catalysts. As is well known to those familiar with the art, the jet fuels that are produced in the presence of various catalysts are not necessarily equivalent in their properties, i.e., some catalysts effect the production of jet fuels having qualities and properties better than those produced in the presence of certain other catalysts. In any event, however, any jet fuel that has been produced by cracking in the presence of hydrogen can be improved by means of the process of this invention.

A number of catalysts that are effective for cracking in the presence of hydrogen are known to the art. Suitable catalysts comprise a mixture of one or more compounds, preferably the oxides or sulfides, of molybdenum, chromium, tungsten, vanadium, iron, nickel, and cobalt; and metallic nickel, iron and cobalt. Very often these materials are used on supports, such as acid treated clays, silica-alumina or other acidic oxides.

As was disclosed in copending application, Serial Num-

5

ber 541,734, filed October 20, 1955, superior jet fuels are produced by cracking in the presence of certain platinum and palladium series metal-containing catalysts.

The catalysts utilizable are those described in copending application, Serial Number 351,151, filed on April 27, 1953, now abandoned; and in the continuation-in-part thereof, Serial Number 418,166, filed on March 23, 1954, now abandoned. 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, and 76-78, inclusive, supported upon synthetic composites of two or more refractory oxides. The carrier is a synthetic composite of two or more oxides of the metals of groups IIA, IIIB and IVA and B of the Periodic Arrangement of Elements [J. Chem. Ed., 16, 409 (1939)]. These synthetic composites of refractory oxides must have an activity index of at least about 25. They can also contain halogens and other materials which are known in the art as promoters for cracking catalysts, or small amounts of alkali metals that are added for the purpose of controlling the activity index of the carrier. Non-limiting examples of the composites contemplated herein include silica-alumina, silica-zirconia, silica-alumina-zirconia, alumina-boria, silica-alumina-fluorine, and the like. The preferred support is a synthetic composite of silica and alumina containing between about 1 percent, by weight, and about 90 percent, by weight, of alumina. These synthetic composites of two or more refractory oxides can be made by any of the usual methods known to those skilled in the art of catalyst manufacture. Examples of methods of preparing them are set forth in copending applications, Serial Numbers 351,151 and 418,166, referred to hereinbefore.

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. $\text{Al}_2(\text{SO}_4)_3$ and 28.6 g. concentrated H_2SO_4 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 percent $\text{Al}_2(\text{SO}_4)_3$ by weight] containing a small amount (0.2 percent by weight) of ammonium sulfate. The thus-exchanged hydrogel bead was water-washed. Then, it was dried in superheated steam (about 280-340° F.) for about 3 hours and, finally, calcined at 1300° F. under a low partial pressure of steam for about 10 hours. The silica-alumina beads were then crushed to pass through a 14-mesh screen and the material retained on a 25-mesh screen (U.S. Standard Screen Series) was used for catalyst preparation.

A portion of the crushed, calcined carrier was subjected to vacuum and then an amount of aqueous solution of chloroplatinic acid was added, which was calculated to fill the pores of the carrier. The concentration of chloroplatinic acid was sufficient to give the desired platinum content in the finished catalyst. The thus-impregnated carrier was then heated in a covered vessel at 230° F. for 20 hours. The catalyst was heated in a nitrogen atmosphere to 450° F. and treated with hydrogen for 2 hours at 450° F. Before it was used, it was activated with hydrogen for 2 hours at 950° F. The

6

catalyst thus prepared contained 0.50% platinum, by weight of the catalyst, and the carrier had an activity index of 46. This catalyst is designated catalyst X.

Another catalyst, catalyst Y, was prepared in a similar fashion, except that it was heated at 230° F. in a covered vessel for 16 hours, instead of 20 hours. It had a platinum content of 0.49 weight percent.

The cracking operation used in the process of this invention is carried out in the presence of hydrogen in amounts, expressed as the molar ratio of hydrogen to hydrocarbon charge, varying between about 2 and about 80, preferably between about 5 and about 50. The liquid hourly space velocity will vary between about 0.1 and about 10, preferably between 0.1 and about 5. When the aforescribed platinum or palladium series metal catalysts are used, the cracking temperature will vary between about 500° F. and about 825° F., preferably between about 600° F. and about 775° F. The hydrogen pressure can vary between about 100 p.s.i.g. and about 3000 p.s.i.g., preferably between about 350 and 2000 p.s.i.g. When the cracking operation, however, is carried out in the presence of other type catalysts, such as the oxides and sulfides of the various metals listed hereinbefore, the temperatures for cracking are higher. Thus, in cracking in the presence of hydrogen with such catalysts, temperatures from between about 600° F. and about 1200° F. are required and, generally, pressures in the order of 500-10,000 p.s.i.g. must be used.

The charge stocks contemplated for use in the process of this invention are hydrocarbon fractions that have an end-boiling point greater than about 650° F. Generally, the charge stocks are derived from petroleum, but other materials can be used, such as, coal oil, shale oil, etc. The charge can have an initial boiling point of 400° F. or higher. Accordingly, the stocks contemplated include a light gas oil which boils between about 400-550° F. and 650-750° F., a heavy gas oil which boils between about 600-650° F. and about 800-900° F., and a vacuum gas oil boiling between about 800-850° F. and about 1100-1200° F. It must be understood however, that the charge can overlap the foregoing boiling ranges. It can even span other ranges that include, for example, medium and heavy gas oils. Another material that is utilizable herein is a whole topped crude petroleum that has been deasphalted. This material is the entire portion of the crude remaining after the light ends have been removed by distillation. Such a fraction, therefore, will boil between about 400° F. up to 1100-1200° F. and higher. Refractory cycle stocks obtained from conventionally cracked stocks are also contemplated. These materials usually boil between about 400° F. and about 850° F.

The presence of even relatively small amounts of nitrogen compounds in the charge stock may interfere 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. The nitrogen compounds also reduce catalyst activity, thus necessitating higher reaction temperature. This produces a more aromatic and less suitable jet fuel.

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 with the platinum or palladium catalysts. Preferably, the nitrogen content should be less than about 0.08 percent, by weight. With certain other catalyst excessive amounts of nitrogen compounds cause aging. Thus, similar precautions should be taken.

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 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 high pressure, in contact with catalysts such as molybdenum or tungsten oxide, nickel 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. Also, a higher nitrogen content can be tolerated in the charge provided that more severe operating conditions, such as higher temperatures, are employed.

The catalyst utilizable in the reforming operation are well known to those skilled in the art. Thus, the catalysts can be oxides or sulfides of the metals of groups IV, V, VI, VII and VIII of the periodic arrangement of the elements, alone or, as is generally the case, supported upon a carrier, such as alumina, spinels, etc. Such catalysts include molybdenum oxide, chromium oxide, cobalt molybdate, and the like. The reforming conditions used with these catalysts include, usually, temperatures of 750–1150° F. and pressures of 50–3000 p.s.i.g.

It is also contemplated to carry out the reforming operation in the presence of hydrogen and of platinum- or palladium-containing catalysts. Such catalysts contain between about 0.05 percent and about 2 percent, by weight of the catalysts, of platinum or palladium, or both, deposited upon supports. Suitable supports, or carriers, include mixtures of two or more refractory oxides, such as silica-alumina, silica-alumina-thoria, alumina-boria, etc. Another type of support utilizable for platinum reforming catalysts is alumina, which may have halogen composited therewith, and which may also contain small amounts of silica. An especially preferred catalyst is described in copending application, Serial No. 420,092, filed March 31, 1954, now U.S. Patent No. 2,849,378. This catalyst comprises platinum or palladium deposited upon silica having composited therewith small amounts of alumina, wherein the amount of alumina added is correlated with the surface area of the catalyst and with the method of preparing it. The reforming conditions used with the platinum- or palladium-containing catalysts include temperatures varying between about 700° F. and about 1000° F., preferably between about 725° F. and about 950° F. The liquid hourly space velocity will vary between about 0.1 and about 10, preferably between about 0.5 and about 4. The hydrogen pressure will vary between about 100 p.s.i.g. and about 1000 p.s.i.g., preferably between about 200 and about 500 p.s.i.g. The molar proportion of hydrogen to hydrocarbon charge will be between about 1 and about 20, preferably between about 4 and about 12.

A number of processes for separating aromatic hydrocarbons from non-aromatic hydrocarbons in naphtha fractions are well known to those familiar with the art. Generally known processes are reviewed, for example, in "Petroleum Processing" for August, 1955 at pp. 1162–3 and 1197–1202. Typical solvent extraction methods and suitable solvents therefor are described in United States Letters Patents Nos. 2,688,645 and 2,773,918. In general, the methods utilizable include (1) sulfur dioxide extraction, (2) extractive distillation with phenol, (3) silica gel adsorption and (4) solvent extraction. The preferred solvents for solvent extraction methods are diethylene glycol and triethylene glycol. Other solvents, however, can be used, such as 1,3-butanediol; 1,4-butanediol; β,β' -oxydipropionitrile; and ethylene carbonate. Specific processing methods and conditions are well known to those skilled in the art.

EXAMPLE 2

The charge stock used in this example was a gas oil distilled from Guico crude. It had the following properties:

Gravity, ° API	26.8
Distillation, vacuum assay, ° F.:	
IBP	602
5%	682
10%	699
20%	722
30%	741
40%	764
50%	781
60%	804
70%	823
80%	844
90%	868
95%	885
Sulfur, wt. percent	0.79
Aniline No., ° F.	184.5
Pour point, ° F.	+105

This gas oil was subjected to cracking in the presence of hydrogen and catalyst X described in Example 1. The pressure used was 1500 p.s.i.g., the hydrogen to oil molar ratio was about 40, and the liquid hourly space velocity was 0.05. The hydrocracking operation was carried out at a temperature of about 784° F. The jet fuel produced was separated into a heavy naphtha fraction and a heavier fraction. Pertinent data and yields of products are set forth in Table I.

EXAMPLE 3

The run described in Example 2 was repeated, except that the pressure was 2000 p.s.i.g. and catalyst Y was used. The jet fuel produced was separated into a heavy naphtha fraction and a heavier fraction. Pertinent data and yields are set forth in Table I.

Table I
Hydrocracking Step

	Example 2	Example 3
Dry gas, Wt. percent	3.0	2.1
Butanes, Vol. percent	9.0	7.1
Light naphtha, Vol. percent	13.5	12.4
Jet fuel (170–480° F.), Vol. percent	73.4	62.2
170–390° F. Cut	54.4	
390–480° F. Cut	19.0	
170–350° F. Cut		33.7
350–480° F. Cut		28.5
480° F. + Product, Vol. percent	21.2	35.1

EXAMPLE 2a

The heavy naphtha cut (170–390° F.) from the hydrocracked jet fuel of Example 2 was reformed in the presence of a platinum-on-alumina reforming catalyst. The operation was carried out under a hydrogen pressure of 500 p.s.i.g., using a hydrogen to oil molar ratio of 10, and a liquid hourly space velocity of 2. The reforming temperature was 895° F. There was obtained a C₆+ reformat having an octane number of 100.8 (F–1+3 cc. TEL). Pertinent data are set forth in Table II.

EXAMPLE 3a

The heavy naphtha cut (170–350° F.) from the hydrocracked jet fuel of Example 3 was reformed in contact with the platinum-on-alumina catalyst under the conditions of Example 2a. The temperature used, however, was 907° F. There was obtained a C₆+ reformat having an octane number of 102.4 (F–1+3 cc. TEL). Pertinent data are set forth in Table II.

Table II
REFORMING STEP

	Example 2a	Example 3a
Dry gas, Wt. percent.....	11.3	12.1
Butanes, Vol. percent.....	8.2	8.8
Pentanes, Vol. percent.....	6.8	5.1
C ₆ + Reformate, Vol. percent, Total.....	72.0	70.6
Based on Hydrocracker Charge.....	39.2	23.8
C ₆ + Reformate O.N. (F-1+3 cc. TEL).....	100.8	102.4

EXAMPLE 2b

The C₆+ reformate obtained in the run of Example 2a was extracted, in 5 stages involving countercurrent extraction, with diethylene glycol. The solvent-to-gasoline volume ratio was 10 and the operation was carried out at ambient temperatures (about 76-80° F.). There were obtained a raffinate and an extract (freed of solvent) having the properties set forth in Table III.

EXAMPLE 3b

The C₆+ reformate obtained in the run of Example 3a was extracted with diethylene glycol, under the con-

process of this invention, to produce high quality jet fuels. This is illustrated in the following examples.

EXAMPLE 2c

The fraction of the jet fuel boiling above 390° F., that was obtained by the operation described in Example 2, was blended with raffinate fraction produced in the operation described in Example 2b. The amount of raffinate so blended was equivalent to the amount of hydrocracked naphtha originally present in the hydrocracked jet fuel (Example 2), i.e., 74 volume percent. The properties of this fuel compared with those of the fuel originally produced (Example 2) are set forth in Table IV.

EXAMPLE 3c

The fraction of jet fuel boiling above 350° F., that was obtained in the operation described in Example 3, was blended with raffinate obtained as described in Example 3b. The amount of raffinate so blended was equivalent to the amount of the hydrocracked naphtha originally present in the hydrocracked jet fuel (Example 3), i.e., 54 volume percent. The properties of the jet fuel so produced and of the original hydrocracked fuel are set forth in Table IV.

Table IV
JET FUELS

Fuel Source	Example 2	Example 2c	Example 3	Example 3c
170-390° F. Portion.....	Hydrocracked.	Raffinate.....		
Vol. percent.....	74	74		
390-480° F. Portion.....	Hydrocracked.	Hydrocracked.		
Vol. percent.....	26	26		
170-350° F. Portion.....			Hydrocracked.	Hydrocracked.
Vol. percent.....			54	54
350-480° F. Portion.....			Hydrocracked.	Raffinate.
Vol. percent.....			46	46
Fuel Properties:				
Gravity, °API.....	50.1	59.7	50.4	56.6
Freezing Point, °F.....	<-76	<-76	<-76	<-75
Sulfur, Wt. percent.....	0.0019	0.0021	0.0020	
Aniline No., °F.....	138.8	146.8	142.2	151.0
Aniline-Gravity Product.....	6,954	8,764	7,167	8,547
Smoke Point, mm.....	30.0	34.2		37.2

ditions set forth in Example 2b. The properties of the raffinate and the extract (freed of solvents) are set forth in Table III.

Table III
EXTRACTION STEP

	Example 2b		Example 3b	
	Raffinate	Extract	Raffinate	Extract
Yield, Vol. percent Total....	35.2	64.8	28.4	71.6
Based on Hydrocracker Charge.....	13.8	25.4	5.8	17.0
O.N. (F-1+3 cc. TEL).....		109.1		109.8
Paraffins, Wt. percent.....	82.8	8.6	85.8	7.4
Napthenes, Wt. percent.....	9.6	2.0	8.8	1.5
Olefins, Wt. percent.....	0.9	0.8	1.5	0.6
Aromatics, Wt. percent.....	6.6	88.6	3.9	90.6
Benzene.....	0.2	4.5	0.1	5.1
Toluene.....	0.7	18.1	0.1	19.9
C ₈ Alkylbenzene.....	1.5	32.0	0.4	35.2
C ₉ Alkylbenzene.....	2.3	23.4	1.3	23.8
C ₁₀ Alkylbenzene.....	1.9	8.7	1.6	6.4
C ₁₁ Alkylbenzene.....		1.9	0.4	0.2

From the data set forth in Table III, it will be noted that the extracts obtained by the operations described in Examples 2b and 3b are rich in monocyclic aromatic hydrocarbons, particularly toluene, xylenes, and trimethylbenzenes. These hydrocarbons are valuable intermediates for preparing a large variety of materials, as those skilled in the art will readily appreciate. It will also be noted that these extracts have extremely high octane numbers (109.1 and 109.8, respectively). Accordingly, if desired and if economically feasible, these extracts can be used as blending stock for the preparation of high octane gasoline, such as by blending with lower octane naphtha. The raffinates are used, in the

From the data set forth in Table IV, it will be apparent that the process of this invention provides jet fuels that are superior to those obtained by hydrocracking alone and also provides valuable aromatic hydrocarbons. The most notable and important improvements lie in the increased Aniline-Gravity Product (a measure of the amount of energy in the fuel) and in the increased smoke point (a measure of the burning quality of the fuel). It will be noted that the fuel properties were improved without raising the freezing point.

In the examples, the hydrocracked naphtha was replaced volume for volume by the raffinate. In this case, there will be some excess higher boiling cut (390-480° F.) which can be used as blending stock for premium diesel fuels or in other jet fuels. It is not necessarily contemplated, however, to blend volume for volume. It is also contemplated to blend the entire higher boiling cut with all the raffinate. Such a fuel may not always meet existing jet fuel distillation specifications. It will be useful, however, in special jet fuel specifications. Likewise, when the entire higher boiling cut is not used, as in the examples, the addition of raffinate still need not be volume for volume, as lesser or greater amounts can be used. Thus, the amount of raffinate blended can vary between about 75 percent and about 125 percent of the volume of the initial hydrocracked naphtha portion it replaces.

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 method for producing a jet combustion fuel and

11

aromatic hydrocarbons which comprises: contacting a hydrocarbon charge stock under hydrocracking conditions in the presence of a hydrocracking catalyst and hydrogen in amounts, expressed in molar ratio of hydrogen to hydrocarbon charge, within the range about 2 to about 80, to convert at least a portion of the hydrocarbon charge into jet fuel boiling range material with an initial boiling point of at least 160° F. and an end boiling point within the range about 450° F. to about 550° F.; separating said jet fuel boiling range material into a cracked naphtha fraction and a hydrocracked fraction having an initial boiling point within the range about 300 to about 400° F. and an end boiling point within the range about 450° F. to about 550° F.; reforming said cracked naphtha fraction in the presence of a reforming catalyst and under reforming conditions to produce a reformat; removing aromatic hydrocarbons from said reformat to produce an aromatic fraction and a non-aromatic fraction; combining said non-aromatic fraction with said hydrocracked fraction having an initial boiling point within the range about 300° F. to about 400° F. and an end boiling point within the range about 450° F. to about 550° F. to produce

12

thereby a finished jet fuel, and recovering aromatic hydrocarbons from said aromatic fraction.

2. The process of claim 1 further limited to: said charge stock having an initial boiling point of at least about 400° F. and an end boiling point greater than 650° F.; said hydrocracking zone employing a catalyst comprising from 0.05 to 20 percent by weight of at least one noble metal of the platinum and palladium series deposited on a synthetic composite of refractory oxides of at least two elements of groups IIA, IIIB and IVA and IVB of the periodic arrangement of elements, said composite having an activity index of at least 25.

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