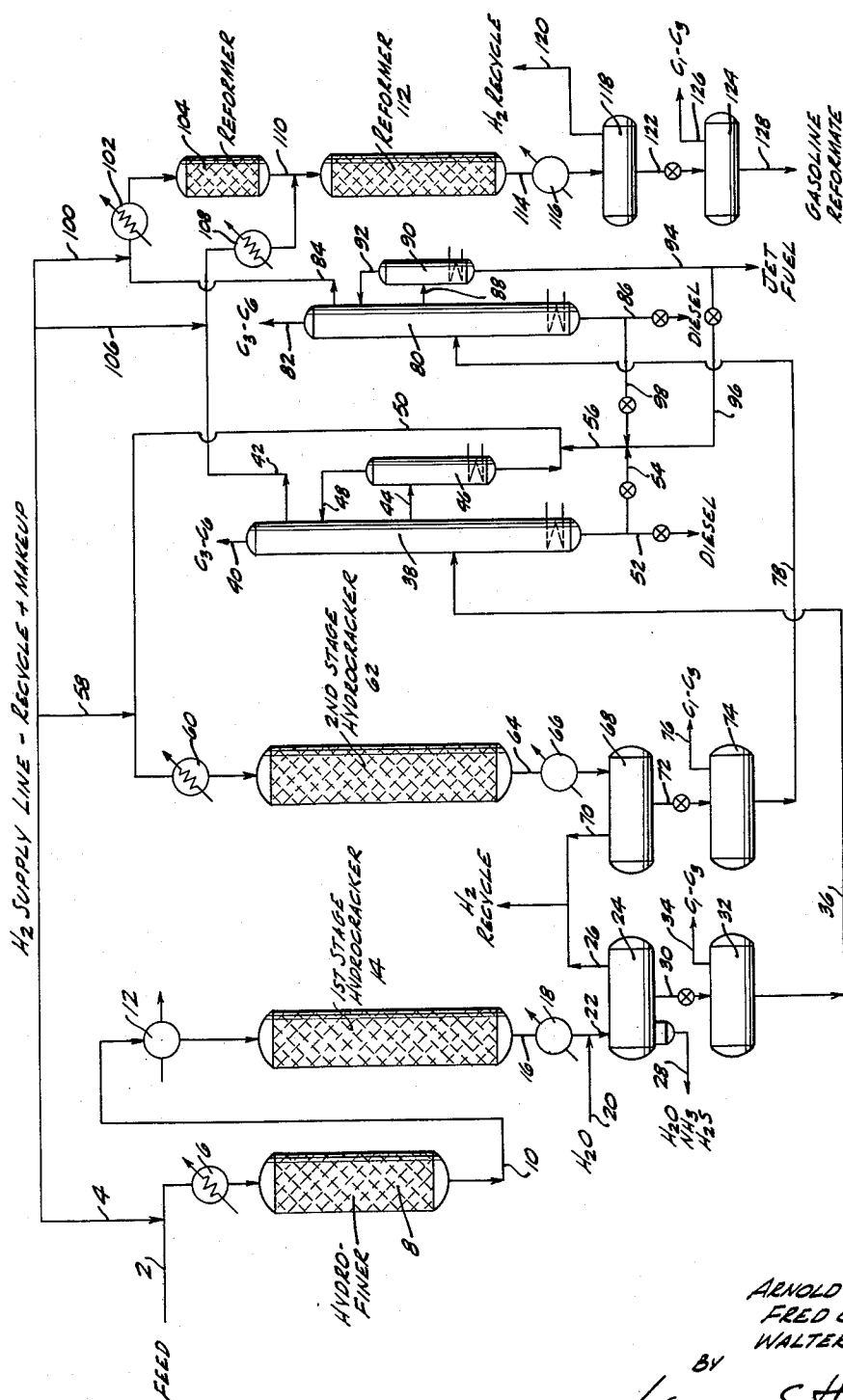


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INVENTORS.
ARNOLD E. KELLEY,
FRED C. WOOD,
WALTER I. BARNET,

BY
Lannas S. Henderson
ATTORNEY.

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MANUFACTURE OF GASOLINE AND JET FUEL
BY HYDROCRACKING

Arnold E. Kelley, Orange, and Fred C. Wood and Walter I. Barnet, Fullerton, Calif., assignors to Union Oil Company of California, Los Angeles, Calif., a corporation of California

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This invention relates to the manufacture of both gasoline and high quality jet fuel by multi-stage catalytic hydrocracking. More specifically, the invention relates to low pressure hydrocracking at below about 3,000 p.s.i.g., wherein the feedstock is first subjected to hydrocracking in the presence of nitrogen base contaminants, and the material not converted to gasoline in the first hydrocracking stage is then subjected to hydrocracking in the substantial absence of nitrogen compounds in a second stage. The product from the second stage is then fractionated separately from the first-stage product, to recover second-stage gasoline, a high quality jet fuel, and optionally a diesel fraction which may be withdrawn from the process or recycled for further hydrocracking in the second hydrocracking stage.

It has been found that, despite the fact that the product from the second hydrocracking stage has been subjected to more total cracking than the first stage product, which seemingly might reduce the proportion of high-quality jet fuel hydrocarbons (paraffins, naphthenes, etc.), the jet fuel fraction recovered from the second stage product contains more paraffins, and exhibits better overall jet fuel characteristics, than does the corresponding jet fuel fraction recovered from the first stage hydrocracking product. It has been found moreover, that a similar difference in jet fuel quality occurs even when the first hydrocracking stage is preceded by an integral hydrofining operation (which would presumably increase the total proportion of saturated hydrocarbons). The gasoline fractions recovered from the respective first and second hydrocracking stages are preferably subjected to catalytic reforming to improve their octane ratings, and it has been found that the first-stage gasoline has a higher initial octane number than the second-stage gasoline, and hence the second-stage gasoline is preferably subjected to a more severe reforming treatment than the first-stage gasoline.

The development of modern jet engines has resulted in the promulgation of many and various specifications for jet fuels. Among such specifications are qualifications relating to freezing point, volatility, stability, corrosiveness to polysulfide-type synthetic rubbers, odor, etc. In addition to these physical and chemical qualifications, various other specifications have been set forth with respect to actual burning qualities, e.g., heat content per pound, smoke point, luminosity of the flame, and the like. Flame luminosity appears to be emerging as one of the more important specifications with reference to burning qualities. A fuel which burns incompletely and produces much smoke will normally generate less usable power per pound than will a fuel which burns with a smokeless flame. Moreover, smoke-producing flames are inherently quite luminous because of the incandescent carbon particles produced during burning. These luminous flames produce relatively more radiant heat with resultant heating of the combustion chamber liner of the jet engine to higher temperatures than would prevail if the engine were operated at the same power output with a non-luminous flame. It has been found in fact that, at the same power output, the engine liner temperature may be as much as 500° F. higher when operating with a luminous flame than when operating with a flame of minimal luminosity.

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To measure the luminosity of flames produced by various fuels, the CFR Luminometer has recently been developed. In this instrument, a fuel sample is burned in a combustion chamber at the same level of luminosity as a reference fuel, and its heat release at that luminosity level is then compared with that of the reference fuel. Thus, a high luminometer number means that a given fuel will produce large amounts of heat at a given flame luminosity, while a low luminosity number means that the fuel will release relatively less heat at that luminosity level. On the CFR Luminometer scale, tetralin has a luminosity number of 0 and isooctane, 100. For an even wider scale, normal heptane can be used, its luminosity number being 220. In general it can be said that the paraffin hydrocarbons have luminosity numbers ranging from 100 to 240, naphthenes and olefins from 40 to 130, and aromatics from —15 to 20. It will thus be noted that the hydrocarbons most desirable in reciprocating piston engines are the least desirable for jet fuels, at least insofar as burning qualities are concerned.

The principal purpose of this invention is to provide an integrated hydrocracking process designed mainly for the production of gasoline, but which can be easily regulated to produce a high-quality jet fuel boiling for example in the 350°–550° F. range. A further objective is to minimize the total reforming capacity required to convert hydrocracked gasoline derived from multi-stage hydrocracking into high octane gasoline. Another objective is to provide maximum flexibility in a multi-stage hydrocracking process, which will permit the refiner to shift readily from jet fuel to gasoline as his market may require. It is a specific object of this invention to provide a hydrocracking process for producing a 350°–550° F. boiling-range jet fuel fraction which will have a luminosity number above about 70. Other objects will be apparent from the more detailed description which follows.

In the succeeding description of process conditions and catalysts to be employed in the various conversion units, it will be understood that the prescribed conditions are set out in order to define an integrated hydrocracking process wherein the jet fuel fraction recovered from the second stage of hydrocracking will inherently be of higher burning quality than the corresponding jet fuel fraction produced in the first hydrocracking stage. In defining these conditions, account is taken of the many complex variables involved, i.e., relative hydrogenating and cracking activity of the catalysts used, temperatures, hydrogen pressures, and the degree of conversion to gasoline-boiling-range materials in each of the two hydrocracking stages. It is perhaps not surprising that high-quality jet fuel fractions can be produced during a hydrogenative cracking process, but in view of the complexity of the variables involved, it was not apparent at the outset that the kinetics of the hydrogenation and cracking reactions occurring in the respective hydrocracking stages, and under the conditions prescribed, would be such that the second stage jet fuel product would be superior to the first stage jet fuel product. Furthermore, inasmuch as the feed to the first hydrocracking stage usually contains basic nitrogen compounds, which are known to inhibit the cracking activity of hydrocracking catalysts relatively more than their hydrogenation activity, and since nitrogen compounds are essentially absent in the second stage, it might have been supposed that the first-stage product would be richer in saturated hydrocarbons in the jet fuel range than would the product from the second-stage.

The feedstocks which may be treated herein include in general any mineral oil fraction having an initial boiling point above the conventional gasoline range, i.e., above about 400° F. and preferably above about 500° F., and having an end-boiling point of up to about 900° F.

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This includes straight-run gas-oils, coker distillate gas oils, deasphalted crude oils, cycle oils derived from catalytic or thermal cracking operations and the like. These fractions may be derived from petroleum crude oils, shale oils, tar sand oils, coal hydrogenation products and the like. Specifically, it is preferred to employ feedstocks boiling between about 400° and 900° F., having an API gravity of 20° to 35°, and containing at least about 20% by volume of acid-soluble components (aromatics+olefins). Such oils may also contain from about 0.1% to 5% of sulfur and from about 0.01% to 2% by weight of nitrogen.

Reference is now made to the attached drawing, which is a flowsheet illustrating the invention in one of its most comprehensive aspects. In the succeeding description, it will be understood that the drawing has been simplified by the omission of certain conventional elements such as valves, pumps, compressors, and the like. Where heaters or coolers are indicated, it will be understood that these are merely symbolical, and in actual practice many of these will be combined into banks of heat exchangers and fired heaters, according to standard engineering practice. The fractionating equipment is merely illustrative of a system providing for maximum flexibility in handling different feedstocks; in actual practice, different feedstocks would require modifications in the fractionating equipment for maximum economy.

In the drawing, the initial feedstock is brought in via line 2, mixed with recycle and makeup hydrogen from line 4, preheated to incipient hydrofining temperature in heater 6, and then passed directly into hydrofiner 8, where hydrofining proceeds under substantially conventional conditions. Suitable hydrofining catalysts include for example mixtures of the oxides and/or sulfides of cobalt and molybdenum, or of nickel and tungsten, preferably supported on a carrier such as alumina, or alumina containing a small amount of coprecipitated silica gel. Other suitable catalysts include in general the oxides and/or sulfides of the group VIB and or group VIII metals, preferably supported on adsorbent oxide carriers such as alumina, silica, titania, and the like. The hydrofining operation may be conducted either adiabatically or isothermally, and under the following general condition:

HYDROFINING CONDITIONS

	Operative	Preferred
Temperature, ° F.	600-850	650-750
Pressure, p.s.i.g.	500-3,000	800-2,000
LHSV, v./v./hr.	0.5-10	1-5
H ₂ /oil ratio, s.c.f./b.	500-15,000	1,000-10,000

The above conditions are suitably adjusted so as to reduce the nitrogen content of the feed to below about 25 parts per million, and preferably below about 10 parts per million.

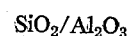
The total hydrofined product from hydrofiner 8 is withdrawn via line 10 and transferred via heat exchanger 12 to first-stage hydrocracker 14, without intervening condensation or separation of products. Heat exchanger 12 is for the purpose of suitably adjusting the temperature of feed to hydrocracker 14; this may require either cooling or heating, depending upon the respective hydrofining and hydrocracking temperatures employed. Inasmuch as first-stage hydrocracker 14 and hydrofiner 8 are preferably operated at essentially the same pressure, it is entirely feasible to enclose both contacting zones within a single reactor, using appropriate temperature control means.

The catalyst employed in reactor 14 may consist of any desired combination of a refractory cracking base with a suitable hydrogenating component. Suitable cracking bases include for example mixtures of two or more refractory oxides such as silica-alumina, silica-magnesia, silica-zirconia, alumina-boria, silica-titania, silica-zirconia-titania, acid treated clays and the like. Acidic metal phosphates such as aluminum phosphate may also be used.

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The preferred cracking bases comprise composites of silica and alumina containing about 50%-90% silica; coprecipitated composites of silica, titania, and zirconia containing between 5% and 75% of each component; partially dehydrated, zeolitic, crystalline molecular sieves, e.g., of the "X" or "Y" crystal types, having relatively uniform pore diameters of about 8 to 14 angstroms, and comprising silica, alumina and one or more exchangeable zeolitic cations.

The foregoing molecular sieve type cracking bases, when compounded with a hydrogenating metal, are particularly useful for hydrocracking at relatively low temperatures of 500°-700° F., and relatively low pressures of 500-1,500 p.s.i.g. It is preferred to employ molecular sieves having a relatively high SiO₂/Al₂O₃ ratio, e.g., between about 2.5 and 6.0. The most active forms are those wherein the exchangeable zeolitic cations are hydrogen and/or a divalent metal such as magnesium, calcium or zinc. In particular, the "Y" molecular sieves, wherein the



ratio is about 5, are preferred, either in their hydrogen form, or a divalent metal form. Normally, such molecular sieves are prepared first in the sodium or potassium form, and the monovalent metal is ion-exchanged out with a divalent metal, or where the hydrogen form is desired, with an ammonium salt followed by heating to decompose the zeolitic ammonium ion and leave a hydrogen ion. It is not necessary to exchange out all of the monovalent metal; the final compositions may contain up to about 4% by weight of Na₂O, or equivalent amounts of other monovalent metals.

As in the case of the X molecular sieves, the Y sieves also contain pores of relatively uniform diameter in the individual crystals. In the case of X sieves, the pore diameters may range between about 6 and 14 Å., and this is likewise the case in the Y sieves, although the latter usually are found to have crystal pores of about 9 to 10 Å. in diameter.

Table 1 below shows the X-ray powder diffraction pattern of the Y sieve. In obtaining the diffraction pattern, standard techniques were employed, utilizing as the radiation source the K α doublet of cobalt ($\lambda=1.7889$ Å.). and a Geiger counter spectrometer with a strip chart pen recorder. The peak heights, I, and the value of the respective Bragg angles were read from the spectrometer chart. From these, the relative intensities, I/I₁, were estimated (strongest peak=100), and the interplaner spacings d(Å.) were calculated from the equation, $\lambda=2d \sin \theta$, λ being the wave length of the source, θ the Bragg angle, and d the interplaner spacing in angstroms.

TABLE 1

d(Å.)	I/I ₁	d(Å.)	I/I ₁
14.6	100	3.30	20
8.85	15	3.32	<10
7.50	10	3.02	<10
5.69	25	2.91	<10
4.75	15	2.85	14
4.37	17	2.76	<10
3.50	<10	2.70	<10
3.76	30	2.63	<10
3.46	<10	2.59	<10
		2.37	<10

Any of the foregoing cracking bases may be further promoted by the addition of small amounts, e.g., 1 to 10% by weight, of halides such as fluorine, boron trifluoride or silicon tetrafluoride.

The foregoing cracking bases are compounded, as by impregnation, with from about 0.5% to 25% (based on free metal) of a group VIB or group VIII metal promoter, e.g., an oxide or sulfide of chromium, tungsten, cobalt, nickel, or the corresponding free metals, or any combination thereof. Alternatively, even smaller proportions, between about 0.05% and 2% of the metals platinum, palladium, rhodium or iridium may be em-

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played. The oxides and sulfides of other transitional metals may also be used, but to less advantage than the foregoing.

In the case of the molecular sieve type catalysts, it is desirable to distribute the hydrogenating metal preferentially in the internal pore areas thereof. This can be accomplished either by forming the sieve crystals in an aqueous medium containing an appropriate, alkali-stable complex of the hydrogenating metal, or by ion-exchanging the hydrogenating metal onto the sieve and reducing to form the free metal and redistribute it into the pores.

A particularly suitable class of hydrocracking catalysts is composed of about 75-95% by weight of a co-precipitated base containing 5-75% SiO_2 , 5-75% ZrO_2 , and 5-75% TiO_2 , and incorporated therein from about 5-25%, based on free metal, of a group VIII metal or metal sulfide, e.g., nickel or nickel sulfide.

The process conditions in hydrocracker 14 are suitably adjusted so as to provide about 20-50% conversion to gasoline per pass, while at the same time permitting relatively long runs between regenerations, i.e., from about 2 to 8 months. For these purposes, it will be understood that temperatures in the high range will be used in connection with pressures in the high range, while the lower temperatures will normally be used in conjunction with lower pressures. The range of operative conditions contemplated for reactor 14 are as follows:

FIRST-STAGE HYDROCRACKING CONDITIONS

	Operative	Preferred
Temperature, ° F	600-850	650-800
Pressure, p.s.i.g.	500-3,000	800-2,000
LHSV, v./v./hr	0.5-10	1-5
H ₂ /oil ratio, s.c.f./b	500-15,000	1,000-10,000

The effluent from hydrocracker 14 is withdrawn via line 16, condensed in condenser 18, then mixed with wash water injected via line 20 into line 22, and the entire mixture is then transferred to high-pressure separator 24. Recycle hydrogen is withdrawn via line 26, and aqueous wash water containing dissolved ammonia and hydrogen sulfide is withdrawn via line 28. The liquid hydrocarbon phase in separator 24 is then flashed via line 30 into low-pressure separator 32, from which flash gases comprising methane, ethane, propane and the like are withdrawn via line 34. The liquid hydrocarbons in separator 32 are then transferred via line 36 to fractionating column 38.

Fractionating column 38 is operated primarily for the purpose of recovering C_7+ gasoline for reforming, and a gas-oil feed for the second-stage hydrocracker. Light gasoline, boiling up to the C_6 range is normally not subjected to reforming, and is hence removed as overhead via line 40. The C_7+ gasoline for reforming is withdrawn as a first side-cut via line 42. In many cases, the entire remaining heavy ends from column 38 may be recovered as bottoms and sent to the second-stage hydrocracker. Normally however it is preferable to withdraw a heavy bottoms fraction from the system in order to prevent buildup of heavy materials boiling above about 700° F. In the modification illustrated, a second side-cut, boiling substantially in the jet fuel range (e.g., 350°-550° F.) is removed via line 44 and transferred to side-cut stripper 46, from which gasoline-boiling-range hydrocarbons are stripped out and returned to column 38 via line 48. The remaining bottoms from stripper 46 constitute the primary feedstock for the second-stage hydrocracking, and is withdrawn via line 50 for that purpose. The bottoms fraction from column 38 may be withdrawn from the system via line 52 and utilized for example as diesel fuel blending stock, or alternatively it may be diverted in part or in whole via lines 54 and 56 to second stage hydrocracker feed line 50 for fur-

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ther conversion to jet fuel and gasoline. The choice of these alternatives depends largely upon market demand for the various products involved.

The total second-stage feedstock in line 50 is then mixed with recycle and makeup hydrogen from line 58, preheated to incipient hydrocracking temperatures in heater 60, and passed into second-stage hydrocracker 62. This feedstock differs considerably from the feed to the first-stage hydrocracker, in that it is substantially free of nitrogen compounds and has a higher gravity. The feedstock is also substantially free of sulfur compounds, and hence the second stage hydrocracker may be operated entirely sweet if desired by simply removing hydrogen sulfide from the recycle gas to that stage. Ordinarily, it is preferred to operate the second stage sweet, in order to maintain the hydrogenating component on the catalyst in a metallic state, the metallic state normally being the most active form for hydrogenation. Moreover, due to the substantial absence of nitrogen compounds, lower temperatures and higher conversion levels can be maintained in hydrocracker 62. The process conditions in hydrocracker 62 are preferably adjusted so as to provide from 30-70% conversion to gasoline per pass. Further, the conversion to gasoline in hydrocracker 62 may be substantially higher, e.g., at least about 10% higher, than in first-stage hydrocracker 14. To achieve these objectives, the hydrocracking conditions should be suitably correlated within the following general ranges:

SECOND-STAGE HYDROCRACKING CONDITIONS

	Operative	Preferred
Temperature, ° F	400-800	500-750
Pressure, p.s.i.g.	500-3,000	800-2,000
LHSV, v./v./hr	0.5-15	1-10
H ₂ /oil ratio, s.c.f./b	500-15,000	2,000-12,000

The catalyst for use in hydrocracker 62 may be of the same general type as previously described for use in hydrocracker 14, except that as noted, it is preferred to maintain the hydrogenating component in the metallic state in hydrocracker 62. At the conversion levels and conditions prescribed for the second-stage hydrocracker, the run length between regenerations can be adjusted to coincide substantially with the run length in reactor 14, e.g., between about 2 and 8 months. In extended runs such as these, it is normally preferable to maintain substantially constant conversion in each stage by incrementally raising the temperature as the activity of the catalyst declines. The rate of catalyst activity decline in reactors 14 and 62 under the prescribed conditions is such that constant conversion in both reactors can be obtained by raising the respective temperatures between about 0.1 and 3° F. per day, on the average. The average temperature in hydrocracker 62 will normally be about 25°-125° F. lower than the average temperature in hydrocracker 14.

The total effluent from hydrocracker 62 is withdrawn via line 64, condensed in cooler 66 and transferred into high pressure separator 68, from which recycle hydrogen is withdrawn via line 70. The condensed hydrocarbons in separator 68 are then flashed via line 72 into low pressure separator 74, from which flash gases are withdrawn via line 76. The liquid hydrocarbon product in separator 74 is withdrawn via line 78 and transferred to second-stage product fractionation column 80, wherein it is fractionated into various gasoline and jet fuel fractions as in column 38. Light gasoline blending stock is withdrawn as overhead via line 82, C_7+ gasoline via line 84, a diesel bottoms fraction via line 86, and a jet fuel side-cut via line 88. The jet fuel side-cut is transferred to a small stripping column 90, from which overhead gasoline hydrocarbons are returned to column 80 via line 92. The entire bottoms from stripper 90 may be withdrawn from the system via line 94 and sent to jet fuel blending and storage facilities. Alternatively, a portion of the jet fuel product

from line 94, may be diverted via line 96 and recycled to second-stage hydrocracker 62 via lines 56 and 50. Also, all or a portion of the diesel fraction withdrawn as bottoms via line 86 may be recycled via lines 98, 56 and 50 to hydrocracker 62. Again it will be understood that the choice of the various alternatives depends largely upon the desired refinery balance and market demands.

The second-stage C_7+ gasoline in line 84 requires a more severe reforming treatment to raise it to a given octane level, in comparison to the first-stage C_7+ gasoline removed from column 38 via line 42. While these two fractions can be blended together and reformed in the same unit, it is preferable where economics permit to treat them separately in order to avoid the loss in liquid yield resulting from overtreating the higher octane product in line 42. This objective may be accomplished by using separate reformers at different temperature levels, space velocities, etc., but in the modification illustrated, a differential space velocity is provided. The low octane gasoline in line 84 is mixed with fresh and recycle hydrogen from line 100, preheated to incipient reforming temperatures in heater 102 and passed through a small pre-reforming unit 104. The higher octane gasoline in line 42 is blended with fresh and recycle hydrogen from line 106, preheated to reforming temperatures in heater 108, and then blended with the effluent from reformer 104 in line 110. The entire blend is then passed into main reformer 112 wherein reforming to the desired octane level is completed. The conditions of reforming in units 104 and 112 are substantially conventional and hence will not be described in detail. Generally the temperatures will range between about 850° and 950° F., pressures between about 300 and 800 p.s.i.g., and the catalysts may comprise a conventional platinum-alumina reforming catalyst, or alternatively other noble metals such as rhodium or palladium on alumina or other carriers may be used. Overall space velocities may range between about 0.5 and 5.0, but preferably the gasoline from line 84 is treated at a space velocity which is being about 0.1 and 0.5 lower than the total space velocity at which the product from line 42 is treated, other treating conditions being the same.

The total effluent from reformer 112 is removed via line 114, condensed in cooler 116, and transferred to high-pressure separator 118, from which hydrogen recycle gas is withdrawn via line 120. The liquid product in separator 118 is flashed via line 122 into low pressure separator 124, from which flash gases are withdrawn via line 126. Gasoline reformat is withdrawn via line 128, and may be sent to blending and storage facilities not shown, where it may be blended with the high octane light gasoline recovered via line 40 and 82.

The following example is cited to illustrate the operation and results of the process as above described in connection with the drawing. This example should not however be construed as limiting in scope:

Example I

In this example, a blend of coker distillate and thermally cracked gas oils derived from California crude oils is utilized as feed. The treatment comprises an initial catalytic hydrofining, with the total hydrofining effluent passing to the first stage of hydrocracking. The first-stage hydrocracking effluent is water-washed and fractionated to recover a C_7 —385° F. gasoline fraction, a 360–510° F. jet fuel fraction and a bottoms fraction, the latter two fractions being fed to the second stage of hydrocracking. The effluent from the second hydrocracking stage is condensed and separately fractionated to recover a C_7 —385° F. gasoline fraction, a 360–510° F. jet fuel fraction and a bottoms fraction, the latter two fractions being in part (75%) withdrawn from the process as jet fuel and diesel fuel products respectively, and in part (25%) recycled to the second stage of hydrocracking.

The significant conditions, specifications and results of the process are as follows:

Initial feedstock:

Boiling range, ° F.	400–750
Acid-solubles, vol. percent	65
Gravity, ° API	23.0
Nitrogen, wt. percent	0.36
Sulfur, wt. percent	2.1

Hydrofining conditions:

Catalyst—3% CoO , 15% MoO_3 on 5% SiO_2 , 95% Al_2O_3 carrier; catalyst pre-sulfided.	
Temperature, average bed, ° F.	705
Pressure, p.s.i.g.	1,500
LHSV	1.0
H_2 /oil ratio, s.c.f./b.	5,000

First-stage hydrocracking conditions:

Catalyst—20% Ni supported on coprecipitated composite of 20% SiO_2 , 30% ZrO_2 , 50% TiO_2 ; final catalyst in sulfided form.	
Temperature, average bed, ° F.	800
Pressure, p.s.i.g.	1,500
LHSV	1.5
H_2 /oil ratio, s.c.f./b.	8,000
Conversion per pass to 0–385° F. gasoline, vol. percent	25

Second-stage hydrocracking conditions:

Catalyst—Same as first stage, except in non-sulfided form.	
Temperature, average bed, ° F.	715
Pressure, p.s.i.g.	1,500
LHSV	1.5
H_2 /oil ratio, s.c.f./b.	8,000
Conversion per pass to 0–385° F. gasoline, vol. percent	42

C_7 —385° F. gasoline products:

	First Stage	Second Stage
Research octane number, clear	64.5	59.5
+3 ml. TEL	83.8	80.1

360–510° F. jet fuel products:

	First Stage	Second Stage
Aniline point, ° F.	122	143
Vol. percent saturates (non-aromatics)	74	93
CFR Luminometer No.	47	71

Second-stage diesel fuel product:

Boiling range, ° F.	500–670
Cetane number	58
Approximate material balances (per 100 bbls. fresh feed):	
Ultimate products—	Barrels
$O-C_6$	19
C_7 —385° F. gasoline:	
First stage	27
Second stage	32
360–510° F. jet fuel	25
500–670° F. diesel fuel	12

The leaded octane numbers of the respective first and second stage C_7 —385° F. gasoline products can be raised to the 100 level by reforming at 925° F. and 600 p.s.i.g. over a conventional 0.5% platinum on alumina catalyst. To accomplish this, the second-stage gasoline is preferably reformed at a total space velocity (LHSV) of about 1.5, while the first-stage gasoline is reformed at 1.8 space velocity.

Example II

Another run was carried out by the same two-stage technique described in Example I, but using a 600° F. end-

point coker gas-oil as feed, and a 0.5% palladium-loaded magnesium "Y" molecular sieve in each hydrocracking stage.

The operating conditions were as follows:

	Hydrofiner	1st Stage Hydrocracker	2nd Stage Hydrocracker
Pressure, p.s.i.g.	1,500	1,500	1,500
LHSV	2	2	1.2
Temperature, ° F.	720	727	565
H ₂ /oil, s.c.f./b.	8,000	8,000	8,000
Conversion/pass		^a 45	^b 50

^a To 400° F. end-point gasoline.

^b To 525° F. —minus material; about 21% conversion per pass to 400° F. end-point gasoline.

The 372–528° F. boiling range jet fuel recovered from the second stage contained only 1% aromatics and 99% saturates. Its luminometer number was 80. The corresponding jet fuel fraction from the first hydrocracking stage was of much lower quality.

Results analogous to those indicated in the foregoing examples are obtained when other hydrocracking catalysts and conditions, other feedstocks and other hydrofining conditions within the broad purview of the above disclosure are employed. It is hence not intended to limit the invention to the details of the example or the drawing, but only broadly as defined in the following claims.

We claim:

1. A process for the manufacture of gasoline and high-quality jet fuel by the hydrocracking of nitrogen-contaminated feedstocks, which comprises:

(1) subjecting a gas oil feedstock boiling above the gasoline range and containing at least about 50 parts per million of nitrogen in the form of organic nitrogen compounds to catalytic hydrofining with added hydrogen to effect decomposition of said organic nitrogen compounds without substantial cracking of hydrocarbons;

(2) subjecting ammonia-containing effluent from said hydrofining, without intervening condensation or separation, to a first stage of catalytic hydrocracking in the presence of a group VIII metal sulfide hydrocracking catalyst, at a temperature between about 600° and 850° F. and under conditions adjusted to give a 20–50% conversion per pass to 400° F. end-point gasoline;

(3) treating the effluent from said first-stage hydrocracking to separate out a first-stage gasoline product, ammonia, and a hydrocarbon residue boiling above said first-stage gasoline boiling range, said residue containing less than about 25 parts per million of nitrogen and comprising a substantial proportion of hydrocarbons boiling in the jet fuel range;

(4) subjecting said hydrocarbon residue plus added hy-

drogen to a second stage of catalytic hydrocracking in the presence of a group VIII free metal hydrocracking catalyst, at a temperature between about 400° and 800° F. under conditions adjusted to give a conversion per pass to 400° F. end-point gasoline which is (a) between about 30% and 70% by volume, and (b) higher than the conversion to gasoline maintained in said first hydrocracking stage;

(5) fractionating the effluent from said second-stage hydrocracking separately from said first-stage hydrocracking effluent, to separate out a second-stage gasoline product and a jet fuel fraction boiling between about 350° and 550° F.;

(6) withdrawing at least a portion of said jet fuel fraction as product and recycling any remaining portion thereof to said second hydrocracking stage;

(7) subjecting the C₇⁺ fraction of said second-stage gasoline to catalytic reforming in the presence of added hydrogen;

(8) subjecting the C₇⁺ fraction of said first-stage gasoline to catalytic reforming in the presence of added hydrogen, but under less severe reforming conditions than the conditions employed for reforming said second-stage gasoline; and wherein

(9) said hydrofining step and each of said hydrocracking stages are carried out at pressures between about 500 and 3,000 p.s.i.g.

2. A process as defined in claim 1 wherein the hydrocracking in said second-stage hydrocracking is conducted at a temperature between about 25° and 125° F. lower than the temperature of said first-stage hydrocracking.

3. A process as defined in claim 1 wherein the initial feedstock to said hydrofining step is a cracked gas-oil boiling between about 400° and 900° F., and containing at least about 20% by volume of acid-soluble components.

4. A process as defined in claim 1 wherein the hydrocracking catalyst in each of said hydrocracking stages contains between about 5% and 25% by weight of nickel, the remainder being made up of a coprecipitated composite of silica, zirconia, and titania.

5. A process as defined in claim 1 wherein the hydrocracking catalyst in each of said hydrocracking stages is a dehydrated, zeolitic molecular sieve of the Y crystal type containing zeolitic cations from the group consisting of hydrogen and divalent metals, and promoted with a group VIII noble metal hydrogenating component.

6. A process as defined in claim 1 wherein said group VIII metal sulfide is palladium sulfide and said group VIII free metal is palladium.

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