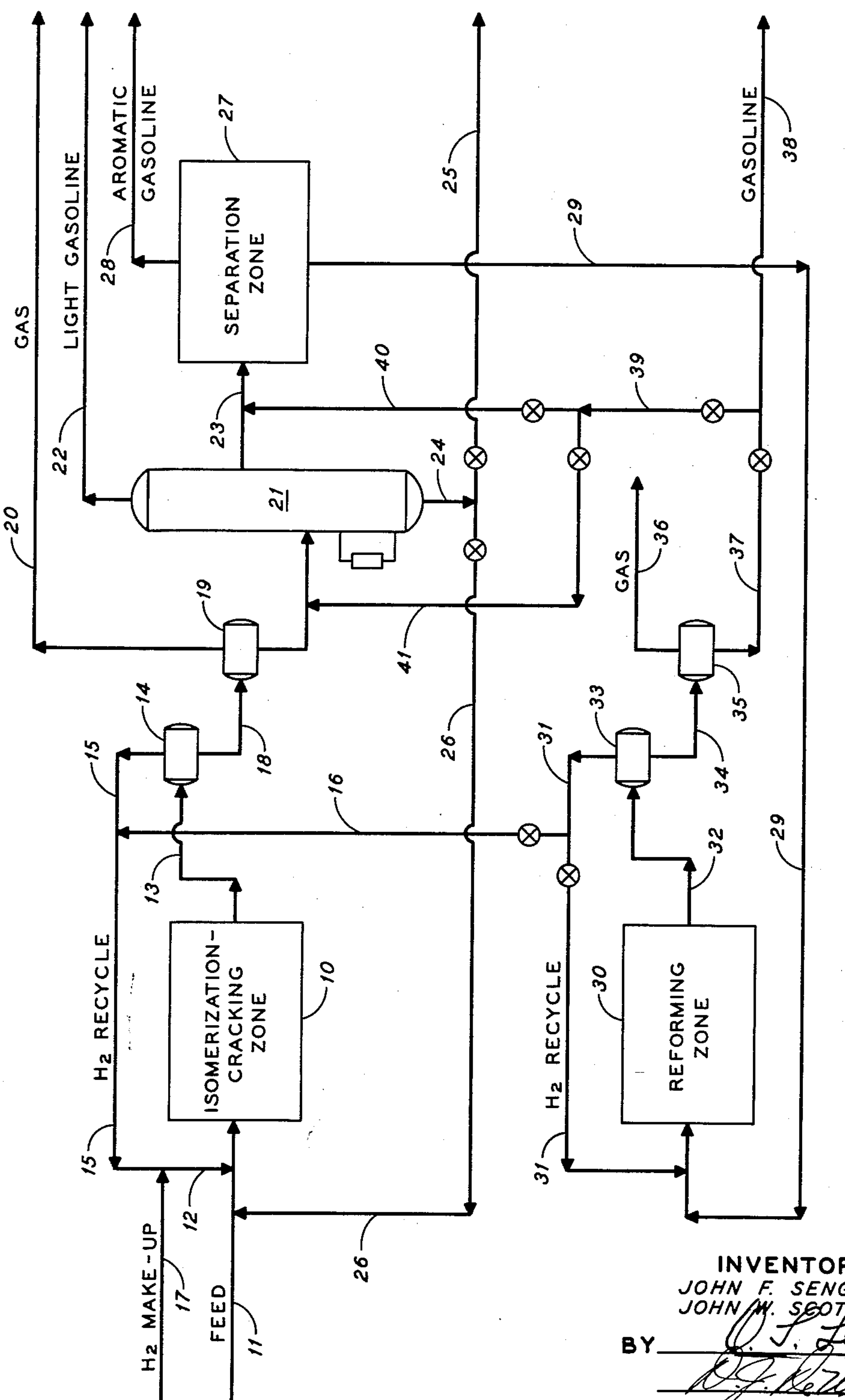
June 6, 1961 J. F. SENGER ET AL 2,987,466

PROCESS FOR THE PRODUCTION OF HIGH OCTANE GASOLINES

Filed June 28, 1956



INVENTORS
JOHN F. SENGER
JOHN W. SCOTT, JR.

BY [signature]
[signature]
ATTORNEYS

United States Patent Office

2,987,466

Patented June 6, 1961

2,987,466

PROCESS FOR THE PRODUCTION OF HIGH OCTANE GASOLINES

John F. Senger, Berkeley, and John W. Scott, Jr., Ross, Calif., assignors to California Research Corporation, San Francisco, Calif., a corporation of Delaware

Filed June 28, 1956, Ser. No. 594,506
7 Claims. (Cl. 208—60)

This invention relates to a process for the catalytic conversion of petroleum fractions to gasolines of high octane rating and good volatility characteristics.

In brief, the process is one wherein a stock such as a naphtha, gas oil, or cycle oil from a cracking unit, along with added hydrogen, is passed at elevated temperatures and pressures through a first conversion zone containing a catalyst made up of one or more hydrogenating components deposited on an active cracking support, following which the effluent is freed of gaseous and lighter gasoline components and is thereafter separated into intermediate and residual fractions. The residual fraction is preferably recycled through said first conversion zone, while the intermediate fraction is substantially separated into aromatic and nonaromatic components. The aromatic components are taken as a product gasoline stream of high quality (especially suitable for use as a blending stock), while the nonaromatic components are passed, again along with added hydrogen and at elevated temperatures and pressures suitable to effect aromatization of the feed, through a second conversion zone provided with a conventional reforming catalyst.

In the preferred practice of this invention the effluent from the reforming zone, after being freed of hydrogen and other normally gaseous components, is also substantially separated into aromatic and nonaromatic components, with the former being recovered as product and the latter being recycled to the reforming zone.

The foregoing process is characterized by a high degree of efficiency, with good per-pass conversions being obtained in the respective conversion zones, and with a high yield of the desired premium gasoline product. In addition to other advantages, the process is particularly characterized by the fact that the over-all gasoline product stream recovered has a higher octane rating than is obtained when the intermediate fraction from the first conversion zone is passed as a whole to the reforming zone.

As stated above, the present invention is adapted to be employed in the conversion to premium gasolines of a wide variety of petroleum fractions. Representative starting materials from which high octane gasolines boiling essentially below 350° F. can be obtained in good yield include petroleum naphthas of straight run, catalytic, or thermal cracked origin and boiling in a range falling between about 175 to 500° F., cycle oils from thermal or catalytic cracking units and including light cycle stocks boiling between about 380 and 600° F. as well as heavier fractions boiling as high as about 750° F., and gas oils boiling within a range falling between about 400 to 750° F. or even higher, as well as mixtures of one or more of the foregoing stocks or fractions thereof. Preferably the feed employed is one containing less than 200 p.p.m. of nitrogen, said levels being reached, when not already present, by a practice of a conventional hydrofining or other pretreatment step. The effluent from this pretreating step can either be fed directly to the initial conversion zone (which zone is referred to herein as the "isomerization-cracking" zone in distinction to the reforming zone), or it can be first subjected to a preliminary fractionation to remove the small amounts of low octane gasoline components which are formed during the more vigorous denitrogenation treatments.

The catalyst employed in the isomerization-cracking zone is one wherein a material having hydrogenating-dehydrogenating activity is deposited or otherwise disposed on an active cracking catalyst support. The cracking component may comprise any one or more of such acidic materials as silica-alumina, silica-magnesia, silica-alumina-zirconia composites, as well as various acid treated clays and similar materials. The hydrogenating-dehydrogenating components of the catalyst can be selected from the various group V through group VIII metals, as well as from the oxides and sulfides thereof, representative materials being the oxides and sulfides of molybdenum, tungsten, vanadium, chromium and the like, as well as metals such as iron, nickel or cobalt and their various oxides. If desired, more than one hydrogenating-dehydrogenating component can be present, and good results have been obtained with catalysts containing composites of two or more of the oxides of molybdenum, cobalt, chromium and zinc. Depending on the activity thereof, the amount of the hydrogenating-dehydrogenating component present can be varied within relatively wide limits of from about 0.1 to 15%, based on the weight of the entire catalyst. Within these limits, the amount of said component present should be sufficient to provide a reasonable catalyst on-stream period at required conversion levels, but insufficient to effect substantial saturation of any except highly substituted and polynuclear aromatic rings under the reaction conditions employed in the isomerization-cracking zone. The latter quality, referred to herein as the "Severity Factor" (S_a), can be evaluated by subjecting the catalyst to a standard test employing as a feed stock a polyalkyl-substituted benzene (or a mixture of such benzenes) wherein the alkyl groups are methyl and/or ethyl, and wherein the feed boils within a range of from about 320° to 420° F., representative stocks being pseudocumene or an aromatic concentrate recovered (as by adsorption) from catalytically cracked or reformed naphthas. The test involves passing the test feed through the catalyst at a liquid hourly space velocity of 2, pressure of 1200 p.s.i.g., and temperature of 800° F., and with approximately 6000 s.c.f. of hydrogen per barrel of feed, for a period of ten hours. The product is then analyzed to determine the percent of the synthetic product portion (i.e., that boiling below the initial boiling point of the feed) which is made up of aromatics (A_p), and then determining S_a by the following equation, wherein A_f is the percent of aromatics in the feed:

$$S_a=\frac{A_f}{A_p}-1$$

The above equation is derived, as shown below, from the following general relationships:

$$S_a=\frac{\text{Aromatics hydrogenation index } (A_h)}{\text{Aromatics cracking index } (A_c)}$$

$$A_h=\frac{\text{Percent aromatics in feed } (A_f) \text{ minus percent aromatics in the product portion boiling below initial boiling point of feed } (A_p)}{\text{Percent aromatics in feed } (A_f)}$$

$$A_c=\frac{\text{Percent aromatics in the product portion boiling below initial boiling point of feed } (A_p)}{\text{Percent aromatics in feed } (A_f)}$$

Combining the above equations:

$$S_a=\frac{A_f}{A_p}-1$$

In the case of a pure aromatic test feed (e.g., pseudocumene), A_f has a value of 100.

In order to be satisfactorily employed in the present invention, the catalyst of the isomerization-cracking zone should have a severity factor (S_a) whose value falls in a range of from about 0 to 5, and preferably of from 0.1 to 2. When S_a has a value greater than 5, there is severe loss in octane number as well as relatively high hydrogen consumption. Such overly active catalysts can, however, be brought into the desired S_a range by suitably reducing the amount of hydrogenating-dehydrogenating component present. While the activity of particular catalysts will vary depending on methods of preparation and with other customary variables, as a general rule exemplary catalysts having satisfactory S_a values are those containing from about 0.5 to 12% molybdenum oxide (preferably 1 to 5% molybdenum oxide), 1 to 5% nickel oxide, mixtures of from 1 to 12% molybdenum oxide and from 0.1 to 5% cobalt oxide, or mixtures of from about 0.5 to 5% each of cobalt oxide and chromium oxide, the said hydrogenating-dehydrogenating components being deposited on an active cracking support such as silica-alumina beads having a silica content of from about 70 to 95%. Thus, a molybdenum oxide catalyst can readily be prepared by soaking the beads in a solution of ammonium molybdate, drying the catalyst for 24 hours at 220° F., and then calcining the dried material for 10 hours at 1000° F. If cobalt oxide is also to be present, the calcined beads can then be similarly treated with a solution of a cobalt compound.

In the following general description of the method in which the present invention may be practiced, reference is had to the figure of the attached drawing which substantially illustrates a suitable refinery flow system. The feed stock to the isomerization-cracking zone **10** is passed via line **11** through the catalyst in said zone, along with added hydrogen from line **12** normally in the form of a recycle stream rich in hydrogen, under elevated conditions of temperature and pressure. More particularly, hydrogen should be supplied in the amount of at least 1500 s.c.f. per barrel of feed, and preferably in the amount of from 3000 to 30,000 s.c.f. per barrel of feed. The temperatures employed in this zone range from about 600 to 900° F. (preferably 650 to 850° F.), with the lower temperatures in the recited ranges being employed in the first part of a given on-stream period, and with the temperatures being raised thereafter as required to maintain the conversion at reasonable levels, i.e., at a level of from about 25 to 75% per-pass based on product produced having an end point lower than the initial boiling point of the feed to the isomerization-cracking zone, said product being referred to herein as "synthetic" product. Other operating conditions to be observed are pressures of at least 600 p.s.i.g. (preferably 1000 to 3000 p.s.i.g.) and space velocities of about 0.1 to 15 v./v./hr. (preferably 1 to 5 v./v./hr.). Under these conditions, the amount of hydrogen which is inherently consumed in the isomerization-cracking zone ranges from about 1,000 to 2,000 s.c.f. for each barrel of feed (including both fresh feed as well as any recycle employed) converted to synthetic product.

The effluent in line **13** from the isomerization-cracking zone is first freed of a hydrogen-rich (usually 85 to 95% H_2) gas stream (line **15**) recovered from a high pressure gas-liquid separator **14** which stream is recycled to the isomerization-cracking zone along with excess, hydrogen-rich recycle gas (line **16**) from the later-encountered reforming zone **30** and additional make-up hydrogen supplied through line **17** as required. The remaining product is then freed of its other, normally gaseous components by passage through line **18** to a low pressure gas-liquid separator **19** from which said components are recovered overhead via line **20**. The balance of the stream is thereafter fractionated (column **21**) to recover a light gasoline product stream (line **22**) having an end point of approximately 200° F., and usually falling in the range of from 165 to 225° F., an intermediate fraction (line **23**) having an end point between about 290 to 440° F., and a bottoms fraction (line **24**). The latter fraction can be withdrawn in whole or in part from the system through line **25** for employment as a component of a diesel or jet fuel, though it preferably is recycled to extinction by being continuously returned to the isomerization-cracking zone via line **26**.

The intermediate fraction from the isomerization-cracking zone is passed through line **23** to a separation unit **27** where the stream is essentially freed of its aromatic components by a practice of conventional techniques employed for this purpose such as by using one or more selective solvents, by using an extractive distillation method (e.g., one employing phenol) or by using a selective adsorbent such as silica gel or the like. Several processes of this latter character are known to in general comprise a countercurrent liquid-liquid contact between the mixed hydrocarbon feed and any of several selective solvents such as the poly-glycols, glycol monoethers, liquid sulfur dioxide, or the like. The separation effected in this unit may, if desired, be relatively gross, or it may be essentially complete, as governed by the nature of particular feed stocks and by the economics of the particular process at hand. Thus, the aromatic fraction recovered via line **28** may contain from about 80 to nearly 100% aromatics, though a preferred aromatics content is from about 85 to 95%. In any event, this stream from line **25** is a gasoline having an octane rating of above about 100, F–1 leaded. It also has good volatility characteristics and is thus well adapted to be used either per se or as a blending stock.

The nonaromatic portion from separation zone **27** is passed, via line **29**, through the catalyst in reforming zone **20**, along with hydrogen-rich recycle gas as supplied through line **31**, at temperatures usually in the range of from about 800 to 1000° F., under pressures in the range of from 200 to 900 p.s.i.g., and at space velocities in the range of from 1 to 3 v./v./hr. Ordinarily from about 2000 to 6000 s.c.f. H_2 are passed over the catalyst with each barrel of naphtha. Two catalysts are commonly employed in catalytic reforming; either molybdenum oxide on alumina, or platinum on alumina. The molybdenum oxide catalysts usually contain 8 to 12% molybdenum oxide disposed on an alumina support, while the platinum catalyst usually contains from about 0.1 to 1% by weight of metallic platinum dispersed on an alumina support. Supports having low cracking activity are deliberately chosen for use in the reforming catalysts. Catalytic reforming as commercially practiced is characterized by a net production of hydrogen. The most significant reactions in the reforming process appear to involve the dehydrogenation of naphthenic hydrocarbons and the dehydrocyclization of paraffins. Ordinarily, the net production of hydrogen in commercial catalytic reforming amounts to from 600 to 1,000 cubic feet of hydrogen per barrel of naphtha charged.

The effluent from reforming zone **30** is passed through line **32** to a high pressure gas-liquid separator **33** from which a hydrogen-rich, gaseous stream is taken overhead through line **31** to be in part recycled to zone **30**, with the balance (representing net production of H_2 in said zone) being sent via line **16** to isomerization-cracking zone **10**. The liquid product from separator **33** is then sent through line **34** to a low pressure gas-liquid separator **35** from which normally gaseous products are taken overhead in line **36**. The liquid product stream (line **37**) from separator **35** is now relatively high in aromatics and has a good octane rating. Accordingly, part or all of said stream may be recovered as a gasoline product stream, line **38**. However, in the preferred practice of this invention said stream is passed through lines **39** and **40** to the aromatics separation zone **27**. Alternatively, the stream in line **37** is passed through lines **39** and **41** to the column **21** to be freed of light gasoline components before being passed to zone **27**. This also gives an opportunity for any heavier portions produced in zone **30** to be reduced in boiling point by return to isomerization-cracking zone **10** along with other bottoms from column **21**.

The benefits to be obtained by a practice of the present invention are apparent from a consideration of the data presented in the following examples. In each example, the procedure first described is one wherein the stock is first passed to the isomerization-cracking zone, with an intermediate fraction from said zone (including all aromatics present therein) being passed to the reforming zone. The results obtained from this method of processing are then compared with those which can be obtained under otherwise similar conditions by removing the aromatics from said intermediate fraction before reforming the same, the effluent from the reforming zone in each case being returned to the fractionating column **21**.

Example I

In this operation a feed stock representing a 50/50 blend as obtained from a thermal cracker and a catalytic cracker, both operating on crude gas oils of California origin, was employed having the following specifications:

Gravity, ° API	42.0
Aniline point, ° F.	107.0
Nitrogen, p.p.m.	2
Aromatics, vol. percent	31
Paraffins, vol. percent	29
Naphthenes, vol. percent	40
Octane, F–1 clear	49.4
Octane, F–1+3 ml. TEL	76.0
ASTM D–86 distillation, ° F.:	
Start	294
10%	319
50%	362
90%	414
End point	440

The above stock, along with 6000 s.c.f. H_2/bbl. feed, was heated to 800° F. and passed at a pressure of 1200 p.s.i.g. and a space velocity of 2 v./v./hr. through the isomerization-cracking zone provided with a catalyst made up of molybdenum oxide (1% by weight as Mo) deposited on a synthetic silica-alumina gel cracking support (TCC beads containing approximately 87% silica and 13% alumina). The effluent from this reaction zone was freed of normally gaseous components, including a recycled, hydrogen-rich stream, and fractionated to obtain a C_5—165° F. gasoline fraction (29.3 vol. percent), an intermediate fraction boiling between 165 and 300° F. (56.7 vol. percent), and a bottoms fraction which was recycled to the isomerization-cracking zone. The intermediate fraction, along with 6000 s.c.f. H_2/bbl. of said feed fraction, was then passed at a space velocity of 2 v./v./hr., a temperature of 900° F. and a pressure of 500 p.s.i.g. through a reforming zone containing Platforming catalyst of Universal Oil Products Company, said catalyst containing 0.3% platinum deposited on an alumina support. As additional product there was recovered a C_5—300° F. fraction from the reforming zone in a yield of 50 vol. percent, this and the other percentages given in these examples being in terms of the volume of fresh feed stock to the isomerization-cracking zone. Combining the C_5—165° F. and C_5—300° F. gasoline fractions obtained above, there is recovered 79 vol. percent of a C_5—300° F. gasoline having an F–1 clear octane rating of 97.9.

In practicing the present invention, the above procedure is modified so as to solvent extract the intermediate (165–300° F.) fraction with a selective solvent (SO_2) to obtain an extract which, when separated from the solvent, has an aromatic content of 90% and a substantially non-aromatic raffinate. The latter comprises the feed to the reforming zone, with the normally liquid portion of the effluent from said zone being returned to the fractionating column from which is taken the intermediate stream to the aromatics separation zone. When operating in this fashion, it is found that the octane number of the combined C_5—300° F. gasoline fraction is substantially increased, the same now having an F–1 clear rating of well above 100. Further, this outstanding increase in octane rating is achieved at a yield loss of not more than about 2%.

Example II

In this operation the process described in the first paragraph of Example I was repeated, except that here the temperature in the isomerization-cracking zone was reduced to 700° F. and the space velocity therein to 1 v./v./hr., while the temperature in the reforming zone was reduced to 850° F. The catalyst in the reforming zone remained unchanged, while that in the isomerization-cracking zone was one comprising cobalt oxide (2% Co) and molybdenum oxide (7% Mo) deposited on TCC beads. In this operation there was obtained an over-all C_5—300° F. gasoline yield of 70 vol. percent, said product having an octane rating of 90.7 F–1 clear.

When the foregoing procedure is modified in accordance with the present invention so as to extract the aromatics from the intermediate fraction supplied to the reforming zone, the octane rating of the combined C_5—300° F. gasoline product is approximately 94.5 F–1 clear, even when a relatively non-severe extracting procedure is employed, i.e., one wherein the aromatics fraction recovered ahead of the reforming zone contains but 85% aromatics.

Example III

In this operation there was employed as feed stock a light catalytic cycle oil of California origin having the following specifications:

Gravity, ° API	26.3
Aniline point, ° F.	108
Nitrogen, p.p.m.	1800
Sulfur, weight percent	0.74
Boiling range, ASTM D–86, ° F.:	
Start	446
5%	470
10%	479
50%	523
90%	586
End point	631

In order to reduce the nitrogen content of this feed to a satisfactory level below about 50 p.p.m., the feed was subjected to a hydrofining operation wherein the stock was passed at an LHSV of 1, a temperature of 770° F. and a pressure of 800 p.s.i.g., along with 12,000 s.c.f. H_2/bbl. of feed, through a catalyst containing molybdenum oxide (9% Mo) and cobalt oxide (2% Co) deposited on alumina. The resulting material was thereafter fractionated so as to strip off the hydrogen sulfide and ammonia gases, leaving a product having the following specifications:

Gravity, ° API	31.0
Aniline point, ° F.	109.0
Nitrogen, p.p.m.	14
Sulfur, weight percent	0.01

The above hydrofined stock, along with 10,000 s.c.f. H_2/bbl. of feed, was then fed through the isomerization-cracking zone at a temperature of 800° F., pressure of 1200 p.s.i.g., and an LHSV of 1, the catalyst in this zone being molybdenum oxide (1% Mo) deposited on TCC beads, as described in Example I. Under these conditions the per pass conversion was approximately 50%, and there was recovered a C_5—180° F. gasoline fraction (25% yield, based on feed to the hydrofining catalyst) having an octane rating of 88, F–1 clear and 100, F–1+3 ml. TEL. An intermediate fraction boiling between about 180 and 380° F. was recovered as feed to the subsequent reforming unit (which intermediate fraction contained approximately 60% of components boiling below 300° F.) while the bottoms fraction boiling above 380° F. was recycled to said zone. The intermediate fraction was then passed along with 6000 s.c.f. H_2/bbl. of feed, at temperature of 900° F., pressure of 500 p.s.i.g. and an LHSV of 2, through a Platforming catalyst in the reforming zone. A C_5—380° F. gasoline fraction was recovered from the reformate stream in a yield of 65%, thus making a total yield of 90 vol. percent based on the original feed to the hydrofining zone. The combined C_5—380° F. gasoline blend produced by this method had an octane number of 95.4 F-1 clear.

As is the case in the runs described in Examples I and II above, the octane level of this C_5—380° F. overall gasoline product can be raised to a value well in excess of 100, F-1 clear, with yield losses of only 2-3% by continuously extracting a 90% aromatics stream from the intermediate fraction fed to the reforming zone with the normally liquid product from said zone being returned either to the aromatics recovery zone or passed into the distillation column from which is obtained the intermediate fraction fed to said recovery zone.

We claim:

1. A process for upgrading a petroleum distillate to a gasoline of high octane rating and good volatility characteristics, which comprises contacting the feed, in the presence of at least 1500 s.c.f. H_2 per barrel of said feed, with a catalyst comprised of a hydrogenating-dehydrogenating component deposited on an acidic, active cracking catalyst support at temperatures between about 600 and 900° F., pressures above about 600 p.s.i.g., and a space rate of from about 0.1 to 15 v./v./hr. in an isomerization-cracking zone, there being consumed in said zone from about 1,000 to 2,000 s.c.f. H_2 per barrel of feed converted to product boiling below the initial boiling point of said feed; freeing the effluent from said zone of hydrogen and other normally gaseous components and, in a fractionating zone, fractionating the remaining normally liquid portion into a light, product gasoline fraction of high octane rating having an end point of from about 165 to 225° F., an intermediate fraction having an end point of from about 290 to 440° F., and a bottoms fraction comprising any material boiling above the end point of said intermediate fraction; separating the said intermediate fraction into an essentially aromatic product fraction and an essentially nonaromatic fraction; contacting said nonaromatic fraction with a reforming catalyst in a reforming zone under reforming conditions; and freeing the effluent from the reforming zone of hydrogen and other normally gaseous components to recover a normally liquid product gasoline fraction characterized by a high octane rating.

2. The process of claim 1 wherein the last-mentioned product gasoline fraction is recycled to the fractionation zone.

3. A process for upgrading a petroleum fraction to a gasoline of high octane rating and good volatility characteristics, which comprises contacting the feed in an isomerization-cracking zone and in the presence of from 3000 to 30,000 s.c.f. H_2/bbl. of feed, with a catalyst comprised of a hydrogenating-dehydrogenating component deposited on an acidic, active cracking catalyst support at temperatures between about 600 and 900° F., pressures above about 600 p.s.i.g., and at a space rate of from about 0.1 to 15 v./v./hr., there being consumed in said zone from about 1,000 to 2,000 s.c.f. H_2 per barrel of feed converted to product boiling below the initial boiling point of said feed; freeing the effluent from said zone of hydrogen and other normally gaseous components, and passing the remainder of the effluent to a

fractionating zone from which are recovered a light, product gasoline fraction having an end point of from about 165 to 225° F., a next-higher boiling, intermediate fraction having an end point of from about 290 to 440° F., and a bottoms fraction boiling above the end point of the intermediate fraction; introducing said intermediate fraction to an aromatics separation zone from which is recovered a product gasoline stream containing from about 80 to 100% aromatics, and a residual, essentially nonaromatic stream; contacting said nonaromatic stream in a reforming zone and in the presence of from about 2000 to 10,000 s.c.f. H_2/bbl. of said stream, with a reforming catalyst at temperatures between about 800 and 1000° F., pressures between about 200 and 900 p.s.i.g., and at space velocities of from about 0.2 to 5 v./v./hr.; freeing the effluent from the reforming zone of hydrogen and other normally gaseous components, and passing the remainder of the effluent to the fractionating zone.

4. The process of claim 3 wherein the last-named effluent remainder is passed to the aromatics separation zone.

5. The process of claim 3 wherein the bottoms fraction from the fractionating zone is returned to the isomerization-cracking zone.

6. A process for upgrading a petroleum fraction to a gasoline of high octane rating and good volatility characteristics, which comprises contacting said fraction in an isomerization-cracking zone and in the presence of from 3000 to 30,000 s.c.f. H_2/bbl. of feed, with a catalyst comprised of a hydrogenating-dehydrogenating component deposited on an acidic, active cracking catalyst support at temperatures between about 650 and 850° F., pressures of from about 1000 to 3000 p.s.i.g., and at a space rate of from about 1 to 5 v./v./hr., there being consumed in said zone from about 1,000 to 2,000 s.c.f. H_2 per barrel of feed converted to product boiling below the initial boiling point of said feed; freeing the effluent from said zone of hydrogen and other normally gaseous components, and passing the remainder of the effluent to a fractionating zone from which are recovered a light, product gasoline fraction having an end point of from about 165 to 225° F., a next-higher boiling, intermediate fraction having an end point of from about 290 to 440° F., and a bottoms fraction boiling above the end point of the intermediate fraction; recycling said bottoms fraction to the isomerization-cracking zone; introducing said intermediate fraction to an aromatics separation zone from which is recovered a product gasoline stream containing from about 80 to 100% aromatics, and a residual, essentially nonaromatic stream; contacting said nonaromatic stream in a reforming zone and in the presence of from about 2000 to 10,000 s.c.f. H_2/bbl. of said stream, with a reforming catalyst at temperatures between about 800 and 1000° F., pressures between 200 and 900 p.s.i.g., and at space velocities of from about 0.2 to 5 v./v./hr.; freeing the effluent from the reforming zone of hydrogen and other normally gaseous components, and passing the remainder of the effluent to the fractionation zone.

7. The process of claim 6 wherein the fresh feed to the isomerization-cracking zone is a cycle oil.

References Cited in the file of this patent

UNITED STATES PATENTS

2,409,695	Laughlin	Oct. 22, 1946
2,697,684	Hemminger et al.	Dec. 21, 1954
2,703,308	Oblad et al.	Mar. 1, 1955
2,736,684	Tarnpoll	Feb. 28, 1956
2,740,751	Haensel et al.	Apr. 3, 1956
2,758,062	Arundale et al.	Aug. 7, 1956
2,769,769	Tyson	Nov. 6, 1956
2,853,437	Haensel	Sept. 23, 1958