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PROCESS FOR UPGRADING CRACKED GASOLINE FRACTIONS

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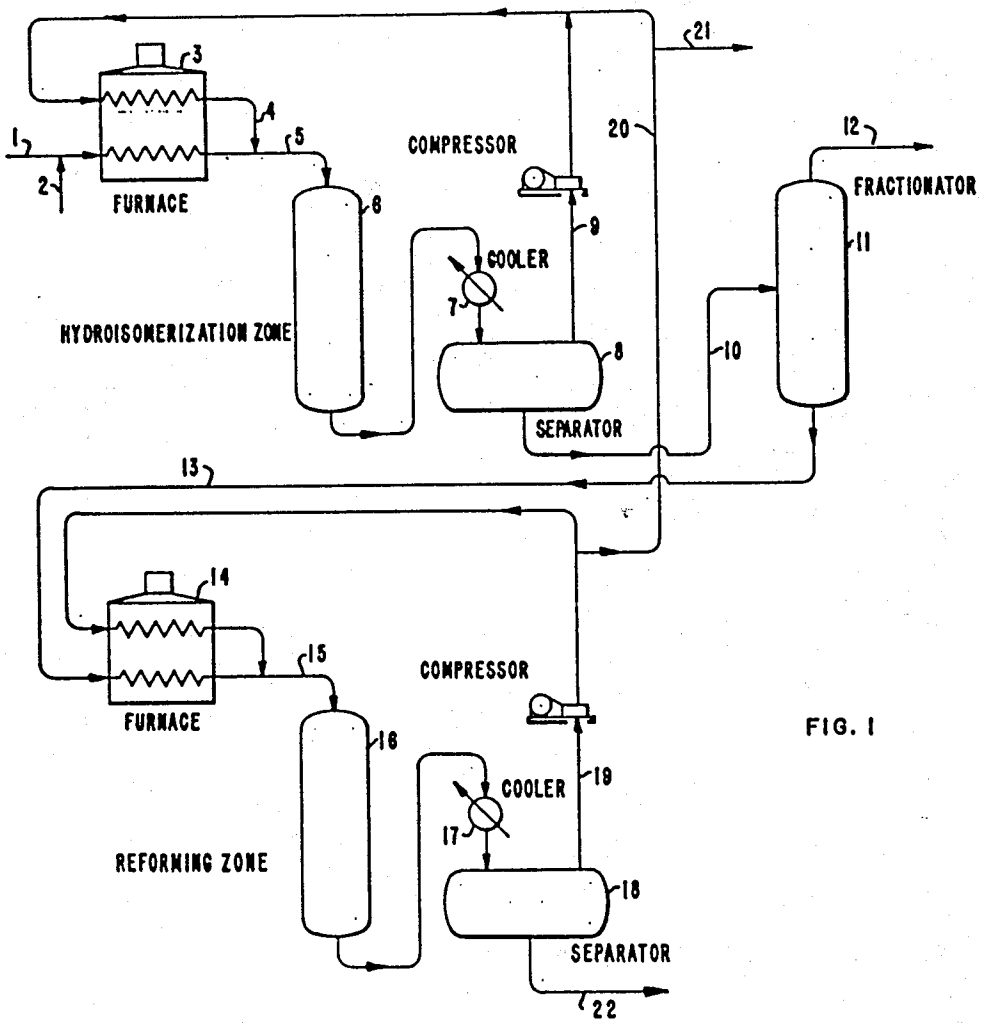

FIG. 1

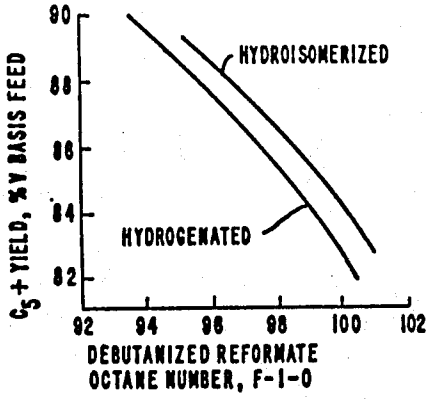

FIG. 2

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PROCESS FOR UPGRADING CRACKED GASOLINE FRACTIONS

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This invention relates to a process for upgrading cracked gasoline fractions and particularly to the upgrading of cracked naphtha by a special hydrogenating treatment followed by catalytic reforming.

Catalytic reforming is a well known and widely used process for upgrading hydrocarbon fractions boiling in the motor gasoline or naphtha boiling range to increase their octane number. In catalytic reforming, a naphtha fraction is contacted at elevated temperatures and pressures together with hydrogen or hydrogen enriched process gas in the presence of solid catalytic materials under conditions such that there is no net consumption of hydrogen and ordinarily there is a net production of hydrogen in the process. The main reactions leading to improvement in octane number are the dehydrogenation and dehydroisomerization of naphthenes, dehydrocyclization of paraffins to aromatic hydrocarbons and the hydrocracking of low octane normal paraffins. Minor reactions which also occur are the isomerization of normal paraffins, and some condensations.

Catalytic reforming operations are ordinarily carried out at temperatures of 850°–1000° F. and a pressure in the range of about 50 to 1000 pounds per square inch. Catalysts for the reforming process comprise a hydrogenation-dehydrogenation component on a suitable carrier such as alumina. Particularly suitable reforming catalysts comprise a small amount, e.g., 0.1–2% of a noble metal, e.g., Pt, Pd, and Rh, supported on a carrier such as alumina, alumina-silica composites, and the like, and frequently promoted with small amounts, e.g., 0.1–3% of chlorine and/or fluorine. Platinum on halogenated alumina is a highly effective and widely used catalyst. However, the older so-called hydroforming catalysts such as compounds of such elements as molybdenum, chromium, cobalt and the like supported on a base, e.g., 10% by weight molybdenum on alumina, are also suitable reforming catalysts. Catalytic reforming processes are described in the "Oil and Gas Journal," 59, No. 14, April 3, 1961, pages 142–150.

Catalytic reforming is usually applied to naphtha fractions, i.e., those having a boiling range of about 185° to 420° F., since these fractions are more susceptible to octane improvement because of their rich naphthene content. Straight-run naphthas are a highly desired feed for upgrading by catalytic reforming because of their high naphthene content, usually about 40% or more, and because of their low octane number. Cracked naphthas such as are obtained from the thermal or catalytic cracking of hydrocarbon oils boiling above the gasoline boiling range, are also suitable for upgrading by the catalytic reforming process. In general, the catalytic cracked naphtha is less suited to catalytic reforming than straight-run or thermal cracked naphtha because of its already relatively high octane number and aromatic content.

The naphtha feed to a catalytic reforming process is usually subjected to a pretreatment such as hydrodesulfurization to remove sulfur and nitrogen compounds. In the case of cracked naphtha, olefins in the cracked stream are saturated by hydrogenation to the corresponding paraffins in addition to the removal of sulfur compounds. The catalyst employed in the hydrodesulfurization process is generally cobalt molybdenum on alumina, which may or may not be stabilized by a minor percent of silica.

These hydrogenation catalysts are widely available commercially. Under the hydrogenation conditions, the naphtha is little affected other than the removal of sulfur and nitrogen and/or saturation of olefins as the case may be.

It has now been found, however, that a cracked naphtha can be greatly improved as a catalytic reforming feed by subjecting the naphtha to a catalytic hydroisomerization process rather than to a conventional hydrodesulfurization process. The invention therefore, is a process for upgrading cracked naphtha wherein the naphtha is passed at an elevated temperature and pressure together with a hydrogen-containing gas over a hydroisomerization catalyst and the hydroisomerized naphtha is then passed at an elevated temperature and pressure over a reforming catalyst at catalytic reforming conditions.

In the hydroisomerization process, the cracked naphtha undergoes a substantial change in composition. In addition to desulfurization and denitrification, a synthesis of ring compounds is observed. This is unexpected for while it is known to convert normal or lightly branched olefins to the corresponding isoparaffins by means of an olefin hydroisomerization catalyst, the improvement in the quantity of cyclic compounds has not been observed heretofore. Hydroisomerization of the normal or lightly branched olefins to highly branched isoparaffins is disclosed in copending application Serial No. 39,818, filed June 30, 1960, by Joost C. Platteeuw and Johannes H. Choufoer.

Various olefin hydroisomerization catalysts can be used within the general and broad scope of the process of the present invention. These catalysts may be defined as comprising a hydrogenation component which is associated with a solid acid-acting support. The hydrogenation component should have a relatively weak hydrogenation activity. One of the main functions of the hydrogenation component is to promote the hydrogenation of highly unsaturated compounds, such as diolefins which are present in the feed or are formed as an intermediate reaction product, which would tend to deposit on the catalyst as a polymerization product. Rapid deactivation of the isomerization function of the catalyst is prevented in this manner and at the same time, through hydrogenation of diolefins to monoolefins which can then take part in the isomerization reaction, a higher yield of branched hydrocarbons is obtained. The use of a component with too strong a hydrogenation action, such as nickel, will result in hydrogenation of the monoolefins before the isomerization component has been able to perform its action.

Highly suitable catalysts comprise a solid acid isomerization catalyst containing a sulfide of one or more of the metals of the left-hand column of group VI (chromium, molybdenum, tungsten) and/or a sulfide of one or more of the metals of group VIII (iron, cobalt, nickel) of the periodic table. By solid acid isomerization catalysts it is meant those which when absorbing butter yellow and other weaker basic indicators, show a color change of these indicators, indicating the transition to the acid form. Suitable acid isomerization catalysts for the dual function catalyst of the invention are compounds of silica and alumina, such as silica-alumina cracking catalyst, compounds of silica and zircoium dioxide, compounds of boron trioxide and alumina, compounds of boron trioxide and silica, compounds of alumina and halogen, such as alumina and chlorine and the like. A catalyst consisting of silica-alumina compounds, in particular those having a silica content of at least 60% by weight and an alumina content of about 1–40% by weight are preferred. Nickel sulfide and/or cobalt sulfide deposited or distended on silica-alumina are particularly preferred olefin hydroisomerization catalysts.

The amount of metal sulfide applied to the acid isomerization catalyst can vary within wide limits and is general-

ly in the range from about 0.5–15% by weight based on the total catalyst. Thus, for example, a catalyst containing silica and alumina, and having a silica content of at least 60% by weight (based on the total catalyst) and to which is applied 1 to 10% by weight of nickel sulfide (based on the total catalyst) is an excellent catalyst for use in the process of the invention. The metal sulfide can be applied to the acid isomerization catalyst, for instance silica-alumina cracking catalyst, by any suitable method known per se. For example, the metal sulfide can be applied by impregnating the acid catalyst with a solution of a salt of the corresponding metal, for instance nickel nitrate followed by drying, calcining and finally sulfiding with hydrogen sulfide or a gas containing hydrogen sulfide.

The olefinic gasoline fractions to be upgraded by the process of the invention are obtained from the catalytic or thermal cracking of hydrocarbon oils boiling above the gasoline boiling range. While it is required that the cracked fraction employed as feed in the process of the invention include at least components boiling within the naphtha boiling range, i.e., boiling in the range from about 185° to 420° F., and preferably about 200° to 390° F., it is generally preferred to use full boiling range cracked gasoline as feed.

The inclusion of light cracked fractions with heavy cracked naphtha as feed has important advantages even though the light fractions are not desired as reforming feed and must be separated from the hydroisomerized naphtha. In the hydroisomerization reaction, light olefins and particularly the normal or lightly branched olefins are converted into isoparaffins. Thus, the olefin content of the light fraction is reduced which is important from the standpoint of air pollution, and the sensitivity (Research Method octane-Motor Method octane) is reduced without excessive loss of Research Method octane.

Moreover, in the hydroisomerization of cracked naphtha, light boiling hydrocarbons, usually referred to as "light-ends," are formed as a result of hydrocracking reactions and/or conversion of olefins to lower boiling isoparaffins. Such light ends are generally unsuitable as a reforming feed. On the other hand, in the hydroisomerization of light cracked gasoline, some "heavy ends" are formed which can be suitably reformed. Therefore, it is better to effect separation of light gasoline fractions from naphtha fractions after rather than before the hydroisomerization reaction.

Hydroisomerization of the olefins in the cracked gasoline fraction is an exothermic reaction and consequently, a large increase in temperature results from the heat of reaction which is liberated. The increase in temperature can be sufficient to promote hydrocracking, which is also an exothermic reaction, and thus lead to so-called runaway hydrocracking. Thus, excessive temperature increases in the reaction zone can result in loss in yield, increased carbonaceous deposits on the catalyst, and possible harm to the catalyst itself. Although, any suitable conventional method of preventing excessive temperature increases in the reaction zone can be employed, such as subdivision of the catalyst into a number of separate beds connected in series with cooling of the reaction mixture between the beds, or by recycling liquid product, it is generally desired to admix with the olefinic hydroisomerization feed a staright-run naphtha fraction as disclosed in copending application, Serial No. 136,795 by Marius 't Hart, filed September 8, 1961. The straight-run naphtha fraction, which is a desired reforming feed fraction, is substantially unaffected in the hydroisomerization process except for desulfurization and denitrification.

The hydroisomerization conversion is carried out in the presence of hydrogen at elevated pressure, preferably at a total pressure not exceeding 1500 p.s.i.g., for instance, in the range of from 150 to 1200 p.s.i.g., and particularly from about 300 to 900 p.s.i.g. The hydrogen partial pressure can vary within wide limits and is preferably

from 50 to 90% of the total pressure. It is not necessary to employ pure hydrogen since hydrogen-containing gases such as hydrogen enriched gases formed in the subsequent reforming step or in the reforming of other hydrocarbon oils are also suitable.

The olefinic cracked fraction is converted at an elevated temperature in the range of from 400° to 900° F. and preferably from 500 to 750° F.

The liquid hourly space velocity of the olefinic cracked fraction to be hydroisomerized is generally in the range of from 0.5 to 20 barrels of liquid hydrocarbons per hour per barrel of catalyst, although lower or higher velocities may also be used.

In the hydroisomerization zone, a substantial portion of the non-cyclic hydrocarbons, primarily the olefin hydrocarbons, are converted into the cyclic compounds, such as naphthenes and/or aromatics. This increase in concentration of cyclic compounds markedly improves the recovered naphtha as a reforming feed stock. Thus, when the hydroisomerized naphtha is subjected to a catalytic reforming process, such as with a reforming catalyst and reforming conditions as mentioned hereinbefore, a higher yield of reformate for a given octane is obtained compared to that obtained from a cracked naphtha which has been hydrotreated in a conventional manner.

The process of the invention will now be illustrated with reference to the drawing wherein FIGURE 1 shows a preferred embodiment and FIGURE 2 shows an advantage obtained by the invention.

Referring to FIGURE 1, a C_5/390° F. cracked gasoline supplied through line **1** is mixed with a straight-run 200°/390° F. fraction from line **2** and heated in furnace **3**. Hydrogen-containing gas which has been heated in the same or a separate furnace is supplied through line **4**, and is mixed with the hydrocarbon feed in line **5**. The mixture of hydrogen and hydrocarbon is passed to reaction zone **6** containing a suitable hydroisomerization catalyst such as nickel sulfide or cobalt sulfide deposited on silica-alumina cracking catalyst. Effluent from the reaction zone is cooled and partially condensed in cooler **7** and is passed to gas/liquid separator **8**. Hydrogen-containing gases are withdrawn from the separator via line **9** for recycle to reaction zone **6**.

Liquid hydriosomerizate is withdrawn from separator **8** through line **10** and passed to fractionation zone **11** wherein a light fraction boiling below about 185° F. and preferably below about 200° F. is separated and removed overhead through line **12**. The light fraction can be worked up as desired, such as by fractionation to recover the butanes, particularly isobutane, with the C_5/185° F. fraction being sent to motor gasoline blending. A 185° F.+, preferably 200° F.+ naphtha fraction is withdrawn from the fractionation zone through line **13** and is heated in furnace **14**. The heated naphtha is mixed with hot hydrogen-containing gas from line **15** and the mixture, at the desired reforming temperature, is passed to reforming zone containing a suitable reforming catalyst, such as a commercial platinum/halogen/alumina catalyst designated as R–8 and supplied by Universal Oil Products Company.

Effluent from the reforming zone is cooled and partially condensed in cooler **17** and is passed to gas/liquid separator **18**. Hydrogen-containing gases are withdrawn from separator **18** through line **19** and at least a part is recycled to the reforming zone. All or a part of the excess gas is supplied via line **20** as make-up to the hydroisomerization zone or is withdrawn for other use via line **21**. Liquid reformate withdrawn from separator **18** via line **22** is worked up in any suitably desired manner, usually such as stabilization to remove light boiling normally gaseous hydrocarbons and to recover a C_5+ reformate product. If desired, the reformate product can be sent to motor gasoline blending as a separate component or can be blended with the light hydroisomerizate fraction.

EXAMPLE I

The starting material was a wide boiling range

(120/365° F.) hydrocarbon fraction comprising on a volume basis approximately 40% light catalytically cracked gasoline, 35% "second-cut" cracked gasoline (a mixture of catalytic and thermal cracked naphtha, predominantly catalytic cracked naphtha), and 25% straight-run naphtha. Properties of the starting material are given below in Table I.

Table I

PROPERTIES OF FEED

API gravity at 60° F	54.8
Group hydrocarbon type, percent v. FIA:	
Saturates and naphthenes	38
Olefins	36
Aromatics	26
Bromine No.	57
Maleic anhydride value	4.1
Nitrogen, p.p.m.	35
Sulfur, p.p.m.	310
Molecular weight	106
ASTM dist., ° F.:	
IBP	120
5%	154
10%	173
30%	216
50%	254
70%	288
90%	329
95%	350
EP	365

For comparative results, separate portions of the starting material were subjected to a conventional hydrogenation process and a hydroisomerization process. The hydrogenation catalyst used was a commercially available catalyst comprising cobalt molybdenum on alumina (14.7% w. MoO_3, 2.8% Co_2O_3/Al_2O_3). The hydroisomerization catalyst was sulfided nickel (10% w.) distended on silica alumina cracking catalyst (approximately 25% Al_2O_3, 75% SiO_2). Operating conditions and typical results for a series of runs are given in Table II.

Table II

COMPARISON OF HYDROGENATION AND HYDROISOMERIZATION

	Hydrogenation	Hydroisomerization
Operating Conditions:		
Temp., F.	668	640
LHSV	1	1.4
Pressure, p.s.i.g.	700	750
Productive Yields, percent v.:		
C_3 and lighter		0.3
iC_4	0.2	1.4
nC_4	0.2	0.2
C_5–182° F.	24.5	25.0
182° F.+	77.1	75.4
Product Properties:		
60–182° F.—		
API Gravity at 60° F.	81.7	80.8
Sulfur, percent w.	0.002	0.005
Bromine No.	0	2
RVP	11.2	12.9
Hydrocarbon Type, percent v.:		
Aromatics	1	1
Olefins	0	1
Paraffins	99	98
Octane Ratings:		
F-1-3	94.0	97.2
182° F.+—		
Pycnometer Density	0.7705	0.7812
Sulfur, p.p.m.	7	50
Molecular Weight	113	116
Bromine No.	0	1
Group Hydrocarbon Type, percent v.:		
Paraffin	38.1	33.4
Naphthenes	34.0	38.3
Aromatics	25.0	27.9
Di Naphthenes	2.9	0.4
Dist., percent w. Overhead:		
IBP	155	158
5%	181	184
10%	197	195
30%	233	232
50%	272	274
70%	297	302
90%	337	340
95%	351	354
EP	409	445

It can be seen from the hydrocarbon type analysis for each product that the hydroisomerized naphtha has an appreciably higher cyclic content and reduced paraffin content compared to the hydrogenated naphtha. This result is attributed at least in part to the cyclization of olefins in the cracked naphtha.

EXAMPLE II

A straight-run naphtha platformer feed was hydroisomerized over nickel sulfide on silica alumina at 675° F., 750 p.s.i.g., and 1.3 LHSV. Analysis of the C_6+ product is compared to that of the straight-run naphtha feed in Table III.

Table III

ANALYSIS OF HYDROISOMERIZATION FEED AND PRODUCT

	Feed	Product
Saturates	42.9	43.2
Naphthenes	42.6	43.1
Aromatics	13.0	12.4
Dinaphthenes	1.5	1.3

Since the slight differences in composition shown in Table III are considered to be within the limits of the analytical method, ring content of non-olefinic naphthas is not affected by hydroisomerization.

A similar experiment was carried out on the hydroisomerization of another straight-run naphtha in admixture of light catalytically cracked gasoline fraction. The mixture comprising 25% v. light cracked and 75% v. straight-run naphtha was passed over nickel sulfide on silica-alumina at about 660° F., 850 p.s.i.g., and 2.0 LHSV. Hydrocarbon type analyses of the hydroisomerization naphtha and the virgin naphtha were identical.

EXAMPLE III

The superiority of hydroisomerized cracked naphtha as a reforming feed is indicated by comparative experiments wherein hydrogenated naphtha and hydroisomerized naphtha are separately reformed over a dehydrogenation catalyst. Each naphtha feed was a composite sample from a series of comparative runs which were described in Example I.

The catalyst used was a commercially available reforming catalyst comprising 0.75% w. Pt, 0.35% w. Cl, 0.35% F/Al_2O_3. The reforming reaction was carried out at 400 p.s.i.g., 2 LHSV, and a H_2/oil molar ratio of 10–11. Temperature was varied to provide a range of severities. The results of these experiments are shown in FIGURE 2 of the drawing which gives the yield-octane relationship for each reformed naphtha. By referring to the drawing, it is clearly seen that when reformed to the same octane rating, the yield obtained from hydroisomerized naphtha is significantly higher than the yield obtained from hydrogenated naphtha.

We claim as our invention:

1. A process for upgrading a cracked gasoline into high octane motor fuel which comprises contacting said cracked gasoline with hydrogen at hydroisomerization conditions in the presence of a hydroisomerization catalyst comprising a sulfide of a metal selected from the group consisting of chromium, molybdenum, tungsten, iron cobalt nickel, and mixtures thereof associated with an acid-acting support, separating the hydroisomerization effluent into a naphtha fraction and a light fraction boiling below the naphtha boiling range, contacting the naphtha fraction with hydrogen at reforming conditions in the presence of a reforming catalyst, and recovering a liquid reformate of high octane number.

2. A process according to claim 1 wherein the cracked gasoline is obtained from the catalytic cracking of hydrocarbon oil boiling above the gasoline boiling range

3. A process according to claim 1 wherein the cracked

gasoline is obtained from the thermal cracking of hydrocarbon oils boiling above the gasoline boiling range.

4. A process for upgrading a cracked gasoline into high octane motor fuel which comprises mixing a cracked gasoline boiling in the range from about C_5 to about 420° F. with a straight-run naphtha, contacting the mixture with hydrogen at hydroisomerization conditions in the presence of a hydroisomerization catalyst comprising a sulfide of a metal selected from the group consisting of chromium, molybdenum, tungsten, iron, cobalt, nickel, and mixtures thereof associated with an acid-acting support, separating the hydroisomerization effluent into a naphtha fraction and a light fraction boiling below the naphtha boiling range, contacting the naphtha fraction with hydrogen at reforming conditions in the presence of a reforming catalyst, and recovering a liquid reformate of high octane number.

5. A process for upgrading a cracked gasoline into high octane motor fuel which comprises contacting said gasoline with hydrogen at hydroisomerization conditions in the presence of a hydroisomerization catalyst comprising a sulfide of a metal selected from the group consisting of chromium, molybdenum, tungsten, iron cobalt, nickel, and mixtures thereof associated with an acid-acting support separating hydroisomerization liquid effluent into a light fraction boiling below about 185° F. and a naphtha fraction boiling above about 185° F., contacting the naphtha fraction with hydrogen at reforming conditions in the presence of a reforming catalyst, and recovering liquid reformate of high octane number.

6. A process according to claim 5 wherein the liquid reformate is stabilized and blended with the light isomerizate fraction.

7. A process for upgrading a cracked gasoline into high octane motor fuel which comprises contacting said gasoline with hydrogen at hydroisomerization conditions in the presence of a hydroisomerization catalyst comprising nickel sulfide deposited on active silica-alumina cracking catalyst, separating hydroisomerization effluent into a light fraction boiling below about 185° F. and a naphtha fraction boiling above about 185° F., contacting the naphtha fraction together with hydrogen at reforming conditions in the presence of a platinum reforming catalyst, and recovering a liquid reformate of high octane number.

8. A process according to claim 7 wherein a straight-run naphtha fraction is mixed with the cracked gasoline and the mixture is hydroisomerized.

9. A process for upgrading a cracked gasoline into high octane motor fuel which comprises mixing a cracked gasoline boiling in the range from C_5 to about 390° F. with a straight-run naphtha boiling from about 200° F.

to 390° F., contacting the mixture with hydrogen at hydroisomerization conditions in the presence of a hydroisomerization catalyst comprising nickel sulfide deposited on active silica-alumina cracking catalyst separating hydroisomerization effluent into a light fraction boiling below about 200° F. and a naphtha fraction boiling above about 200° F., contacting the naphtha fraction together with hydrogen at reforming conditions in the presence of a platinum reforming catalyst, and recovering a liquid reformate of high octane number.

10. A process for upgrading a cracked gasoline into high octane motor fuel which comprises separating said cracked gasoline into a light fraction and a naphtha fraction contacting said naphtha fraction with hydrogen at hydroisomerization conditions in the presence of a hydroisomerization catalyst comprising a sulfide of a metal selected from the group consisting of chromium, molybdenum, tungsten, iron, cobalt, nickel, and mixtures thereof associated with an acid-acting support, recovering a hydroisomerized naphtha fraction, and contacting the hydroisomerized naphtha together with hydrogen at reforming conditions in the presence of a reforming catalyst.

11. A process according to claim 10 wherein a straight-run naphtha is mixed with the cracked naphtha and the mixed naphtha is hydroisomerized.

12. A process for upgrading a cracked gasoline fraction into high octane motor fuel which comprises contacting a cracked naphtha fraction with hydrogen at hydroisomerization conditions in the presence of a hydroisomerization catalyst comprising a sulfide of a metal selected from the group consisting of chromium molybdenum, tungsten, iron, cobalt, nickel, and mixtures thereof associated with an acid-acting support, recovering a hydroisomerized naphtha, and contacting the hydroisomerized naphtha fraction with hydrogen at reforming conditions in the presence of a reforming catalyst, and recovering a liquid reformate of high octane number.

13. A process according to claim 1 wherein the hydroisomerization catalyst is cobalt sulfide deposited on active silica-alumina cracking catalyst.

14. A process according to claim 1 wherein the hydroisomerization catalyst is nickel sulfide deposited on active silica-alumina cracking catalyst.

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