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PROCESS FOR UPGRADING A WIDE RANGE GASOLINE

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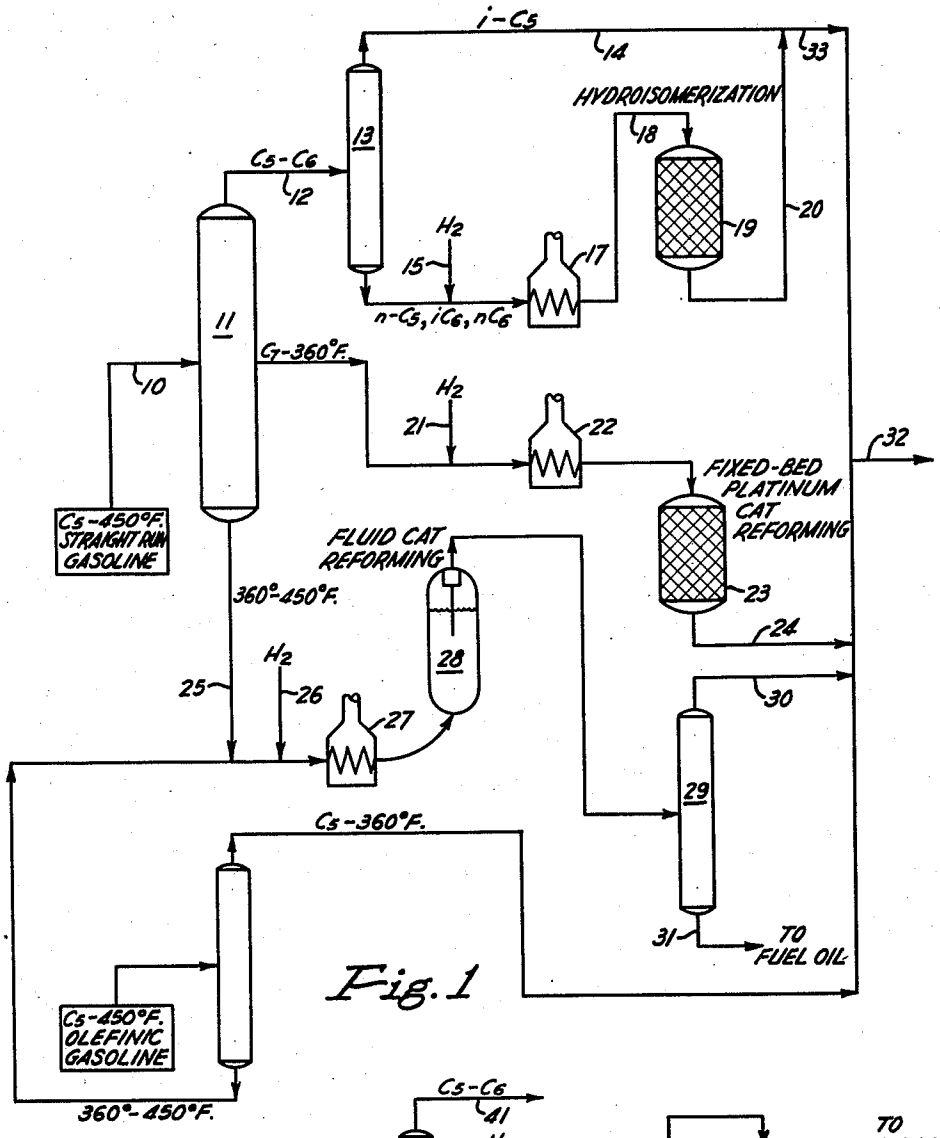

Fig. 1

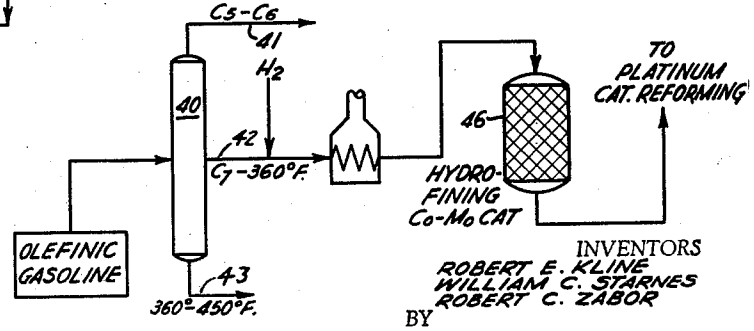

Fig. 2

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PROCESS FOR UPGRADING A WIDE RANGE GASOLINE

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This invention relates to a process for improving the value of gasoline fractions and more particularly to a process comprising separation of gasoline range hydrocarbons into fractions and selective treatment of such fractions and blending of products to obtain motor fuels of high octane rating.

The improvement of gasoline octane ratings is a matter of great importance to petroleum refiners. In the past, gasolines have been produced by catalytically reforming a relatively narrow range straight run fraction and blending the reformate with other relatively high octane fractions such as catalytically cracked gasoline. Normally, the narrow gasoline range fraction is processed in a single type of reforming process that results chiefly in increased aromatic content of the fraction.

There has existed for some time a need for a unified system of treatments for upgrading the entire pool of straight run gasoline and/or olefinic gasolines, such as catalytically or thermally cracked gasolines. We have now developed a combination process for treating the entire refinery pool of gasoline range hydrocarbons whether it consist solely of straight run gasoline or of straight run and cracked gasolines. Our process is characterized by the separation of a full range gasoline fraction into smaller fractions that are amenable to particular treatments, each of these selected treatments cooperating in a unique way with the treatments of other fractions.

In general, our process comprises fractionating a full range straight run gasoline fraction to obtain a light paraffinic fraction containing substantially all of the C_5 and C_6 paraffins of the charge stock, a middle fraction including the C_7 hydrocarbons and extending to an end point of about 360° F. and a heavy fraction having an initial boiling point of about 360° F. n-Pentane and n-hexane of the light paraffinic fraction are subjected to isomerization by contact with a supported platinum catalyst at a temperature from 600 to 850° F., a liquid-hourly space velocity greater than 5 volumes of hydrocarbon per volume of catalyst per hour (hereinafter abbreviated vol./vol./hr.) and a low hydrogen concentration of below about 1000 standard cubic feet per barrel of hydrocarbon (hereinafter abbreviated s.c.f./bbl.) and a product of increased branched chain paraffin content is recovered. The middle fraction is reformed by contact with a platinum-alumina catalyst at a hydrogen concentration greater than 3000 s.c.f./bbl., a space velocity below 4 vol./vol./hr., and a temperature above 850° F. and a reformate of increased aromatics content is recovered. The heavy gasoline fraction is subjected to hydroreforming in the presence of a fluidized molybdenum oxide catalyst at a hydrogen concentration greater than 3000 s.c.f./bbl., a temperature about 850° F. and a space velocity below 3 vol./vol./hr. and two products are recovered, a gasoline of lower average molecular weight and higher aromatic content than the charge to the fluid catalytic hydroreforming treatment and a heavier residual product. The gasoline range products of each of the three catalytic

treatments are then blended to produce a gasoline product boiling from about 100 to 400° F., and having an unleaded Research method octane rating of about 90 or above.

Our process can be applied to the treatment of the entire refinery gasoline pool, including straight run gasolines and olefinic gasolines obtained from cracking processes and the like. In this event the process will include the procedure of fractionating a full range (e.g., C_5—450° F.) olefinic gasoline to obtain a light fraction and at least one heavier fraction. The light fraction containing C_5 and C_6 hydrocarbons is blended without further treatment with the gasoline product obtained by treatment of straight run gasoline. A heavier fraction is mixed with the heavy straight run fraction charged to the fluid catalytic hydroreforming stage. In an especially preferred embodiment an intermediate fraction of the olefinic gasoline is subjected to a mild refining treatment comprising contact with a hydrogenating catalyst at a temperature below 750° F. a space velocity from 3 to 10 vol./vol./hr., and a hydrogen concentration from 500 to 2000 s.c.f./bbl. whereby to saturate the olefins and reduce the sulfur content of the fraction. The resulting product is then mixed with the straight run feed stock for platinum-catalyst fixed-bed reforming.

Our process will be described in more detail by reference to the drawings, of which:

Figure 1 is a flow diagram of one embodiment of our process in which the feed stock comprises full range straight run and olefinic gasoline.

Figure 2 is a flow diagram of a modification of our process in the charging of olefinic gasoline.

In the modification of our process indicated by the flow diagram of Figure 1 the charge stock comprises full range straight run gasoline and olefinic gasoline which range in composition from C_5 hydrocarbons to 450° F. end point material. The straight run gasoline feed stock is introduced by line **10** to a fractionating column **11**, which is a standard multidraw bubble tray fractionating column. Three products are withdrawn from column **11**: an overhead light gasoline fraction consisting of C_5 and C_6 hydrocarbons; a middle fraction consisting of C_7 hydrocarbons to 360° F. end point material; and a heavy fraction boiling from about 360 to 450° F. The light fraction is passed by line **12** to a second fractionating column **13** in which isopentane is separated from n-pentane and the hexanes. Isopentane is withdrawn overhead by line **14** and is recovered for blending with the final product. The bottoms from column **13**, consisting of n-pentane, n-hexane and branched chain hexanes, is mixed with hydrogen from line **15**, preheated to about 800° F. in the heater **17** and introduced by line **18** to the hydroisomerization reactor **19**. This reactor contains a stationary bed of pelleted catalyst consisting of a minor amount of platinum deposited on a halogen-promoted alumina support.

The C_5—C_6 paraffinic charge stock to the isomerization reactor **19** is treated under hydroisomerization conditions described in the patent application of William C. Starnes and Robert C. Zabor, Serial No. 508,980 filed May 17, 1955, now U.S. Patent 2,831,908.

Typical hydroisomerization conditions for the reactor **19** include an average reactor temperature of about 800° F., pressure of about 500 pounds per square inch gauge (hereinafter abbreviated as p.s.i.g.), a liquid-hourly space velocity of about 8 volumes of hydrocarbon per volume of catalyst per hour and a hydrogen concentration of about 500 standard cubic feet per barrel of hydrocarbon. The catalyst in this embodiment consists essentially of about 0.5 weight percent platinum, 1.0 weight percent fluorine and the balance predominantly alumina. A product rich in branched chain C_5 and C_6 paraffins is re-

covered from reactor 19 by line 20. Hydrogen is separated from the hydrocarbon product and is recycled to the reactor feed in advance of the preheater. The high octane hydrocarbon product, after stabilization and fractionation is recovered for blending to form the final gasoline product.

The composition of the middle fraction withdrawn from column 11 ranges in this specific embodiment from C_7 to 360° F. end point material. The middle fraction is admixed with fresh or recycled hydrogen introduced via line 21. The hydrocarbon-hydrogen stream is preheated in preheater 22 to a temperature of about 900° F. and is introduced into the reforming reactor 23. The reactor 23 contains a stationary bed of pelleted platinum on alumina catalyst. In this specific embodiment the fixed-bed reforming catalyst consists essentially of 0.4 weight percent platinum, 0.4 weight percent fluorine and the balance substantially entirely alumina.

The catalytic contact in reactor 23 is carried out at lower space velocity, higher hydrogen concentration and higher temperature than the contact in reactor 19. The space velocity of the feed to reactor 23 is from 1 to 4 volumes of hydrocarbon per volume of catalyst per hour. The hydrogen concentration is above 3000 s.c.f./bbl. and the reactor inlet temperature is about 900° F. The drawing, for simplicity, shows a single reactor 23 for the reforming of the middle fraction over a fixed-bed platinum-alumina catalyst. However, as we will explain more fully hereinafter, this reforming stage can be carried out in a series of two or more reactors, each having a preheater.

The effluent from reactor 23 is withdrawn via line 24. The normally liquid hydrocarbons are separated from hydrogen and light hydrocarbon gases by conventional means not shown in the drawing and hydrogen is recycled to the charge in advance of the preheater 22. The entire normally liquid hydrocarbon product is of the gasoline boiling range, i.e., end point no higher than about 400° F. It is a high octane product of about the same average molecular weight but of higher aromatic content than the middle fraction charged to the reactor 23 and without further fractionation can be blended in its entirety with the final gasoline product withdrawn via line 32.

The heavy fraction withdrawn from column 11 via line 25 is the residue of the straight run gasoline feed stock boiling above about 360° F. This heavy fraction, after being mixed with hydrogen, from line 26 and preheated in the heater 27 is introduced to the fluid catalytic hydroreforming reactor 28. The reactor 28 contains a fluidized bed of finely divided catalyst consisting of molybdenum oxide supported on alumina. Reaction conditions include: temperature 950° F., pressure 500 p.s.i.g., liquid-hourly space velocity 1 vol./vol./hr. and hydrogen concentration 6,000 s.c.f./bbl. Reactor 28 has associated with it a catalyst regeneration vessel, not shown in the drawing through which the spent fluidized catalyst from the reactor is continuously circulated. The catalyst is regenerated by combustion and a stream of hot regenerated catalyst is continuously returned to reactor 28 in a manner well known in the art. A reformed product of substantially lower average molecular weight and higher octane number than the heavy fraction charged is withdrawn overhead from reactor 28. After separation of the normally liquid hydrocarbons from light hydrocarbons and hydrogen, the latter being recycled to the reactor in advance of the preheater, the heavy fraction reformate is introduced to the fractionating column 29. A high octane gasoline overhead product is recovered via line 30 for blending to form the final gasoline product. The bottoms, which boils above about 400° F. is passed to fuel oil blending via line 31.

The gasoline product withdrawn by line 32 is a blend of the entire normally liquid hydrocarbon content of the isomerate and straight run isopentane from line 33, the entire normally liquid hydrocarbon content of the fixed-bed platinum catalyst reformate from line 24 and the light fraction of the fluid catalytic reformate from line 30. The blend has a leaded octane rating (Research, +3 cc. TEL/gal.) of above 95 and a boiling range from about 100 to 400° F.

The particular embodiment of our process that we have described with reference to the drawings can be varied somewhat. We will now discuss ways in which the process can be varied without departing from the spirit of the invention.

We have disclosed separating straight run gasoline into three fractions: a C_5—C_6 fraction, a C_7—360° F. fraction and a 360° F. to end point fraction. An essential feature of our invention is that the C_5 and C_6 paraffins are separated from higher boiling components and are upgraded by hydroisomerization rather than by reforming as applied to the higher boiling fractions. Since the light fraction contains almost all of the C_5 and C_6 paraffins, the lightest components of the middle fraction are the C_7 hydrocarbons. The middle fraction, within the practical limits of refinery separation, is substantially free of hexanes and lighter components. The middle fraction, in accordance with the invention, is reformed over a fixed-bed platinum-alumina catalyst. An important feature of our invention is that the charge to this stage contains only components for which this type of reforming is particularly suited. It contains no more than minor and harmless amounts of components, such as olefins, sulfur compounds or high boiling hydrocarbons, that would rapidly inactivate the fixed-bed platinum catalyst if present in sufficiently high concentrations. Preferably, the end point of the middle fraction is about 360° F. Satisfactory results can be obtained with a middle fraction having an end point somewhat lower than 360° F., for example, as low as 320° F. However, the end point of the middle fraction must not be substantially above 360° F. The reason is that naphthenes of the middle fraction are dehydrogenated to aromatics in the fixed-bed reforming stage. The reformate therefore has a higher end point than the reforming charge stock. If the end point of the middle fraction which is the reforming charge stock is much above 360° F. the end point of the reformate will be too high for gasoline blending. Therefore, it would be necessary to refractionate the reformate to obtain a fraction suitable for gasoline blending. An advantage of our process is that the reactor effluent from the fixed-bed reforming stage, after being separated from light gases, can be passed directly to final gasoline product blending without further fractionation.

The heavy fraction from the distillation of the straight run gasoline comprises all material boiling above the end point of the middle fraction. Therefore, the initial point of the heavier fraction is preferably about 360° F. but can vary from about 320° F. to 360° F. A significant feature of the heavy fraction is that it contains materials that would not be satisfactory for charging to a fixed-bed platinum catalyst reforming process but which can be satisfactorily treated in fluid catalytic reforming. For convenience, we have referred to the heavy fraction as a 450° F. end point fraction and this is the preferred end point. However, in accordance with our invention the heavy fractions can range in end point from about 410 to 500° F.

We have described one particular combination of reaction conditions for the hydroisomerization of the light straight run fraction. However, as already mentioned, other conditions within the ranges of hydroisomerization conditions described in said patent application Serial No. 508,980, now U.S. Patent 2,831,908, can be used. These conditions include, in comparison to catalytic reforming conditions, a low hydrogen concentration, a high space velocity and a moderate temperature.

The hydroisomerization process employing this com-

bination of conditions is particularly adapted for charge stocks highly concentrated in aliphatic pentanes and hexanes (i.e., containing at least 85 volume percent aliphatic pentanes and/or hexanes) and is characterized in its results by a high space-time-yield of the desired branched chain paraffins. The hydrogen concentration is much lower than is used in catalytic reforming of highly naphthenic stocks, namely, below about 1000 s.c.f./bbl. However, the hydrogen concentration must be appreciable. If it is too low the catalyst will be rapidly deactivated by carbonaceous deposits. Therefore, the hydrogen concentration is less than about 1000 s.c.f./bbl. but greater than the concentration corresponding to rapid catalyst deactivation and in any event greater than about 50 s.c.f./bbl.

The liquid-hourly space velocity is at least 5 vol./vol./hr. and preferably is at least 8 vol./vol./hr. With the high rate of isomerization obtained with the stated low hydrogen concentration, satisfactory conversion to branched chain isomers can be obtained at very high space velocity, e.g., 25 vol./vol./hr. or higher. The average reactor temperature in the hydroisomerization stage is considerably below conventional temperatures for catalytic reforming and will in no event be higher than 850° F. The exact temperature will depend on the particular charge stock and on the activity of the particular platinum-alumina catalyst. A highly active catalyst, promoted with a high concentration of fluorine, will give satisfactory conversions at temperatures as low as about 600° F. Accordingly, the temperature can range from 600 to 850° F. The reactor pressure should be above about 200 p.s.i.g. and preferably is 200 to 600 p.s.i.g.

The platinum-alumina catalyst for the hydroisomerization stage comprises a minor amount of platinum and a major amount of alumina. The catalyst can be in the form of irregular granules or of particles of uniform size and shape prepared by pelleting, extrusion or other suitable methods. The platinum content can be from 0.1 to 5 percent by weight but preferably is from 0.3 to 0.6 percent by weight. The catalyst contains a minor amount, for example, from 0.1 to 10 percent by weight of chlorine and/or fluorine and/or other activating components. The halogen or other activating components can also be included in the feed to the process. The catalyst may contain a minor amount, for example, 5 percent or less, of silica which serves as a stabilizer.

Figure 1 shows an embodiment of our process in which the C_5 and C_6 fraction is distilled to remove isopentane, after which the rest of the fraction, consisting of n-pentane, n-hexane and the branched chain hexanes, is charged to the hydroisomerization stage. However, a number of variations are possible in processing the C_5 and C_6 paraffins. The essential step is that n-pentane and n-hexane are hydroisomerized in contact with a platinum-alumina catalyst under the described reaction conditions, but it is not essential that they be hydroisomerized in the same reactor. They can be separated and hydroisomerized separately. It is also within the scope of the invention to recycle low octane number components of the hydroisomerization product to the hydroisomerization reactor **19**. Thus, the reactor effluent of line **20** can be fractionally distilled or subjected to molecular sieve separation or to other separation techniques to obtain a fraction enriched in n-pentane, n-hexane and/or methylpentanes. This fraction is then recycled to the hydroisomerization feed line **18** while the fraction enriched in isopentane and dimethyl butanes is passed via line **33** to final product blending.

We have described a specific combination of reaction conditions for the stage in which the middle fraction is reformed in contact with a fixed-bed platinum catalyst. The processing conditions for this stage can also vary somewhat. Thus, reaction conditions for the second stage include a temperature from 850 to 950° F., a pressure from 300 to 700 p.s.i.g., a liquid-hourly space velocity from 1 to 4 vol./vol./hr. and a hydrogen to hydrocarbon ratio from 3,000 to 10,000 s.c.f./bbl. These ranges may in part overlap the ranges of conditions suitable for the isomerization stage. However, for any specific combination of conditions for the isomerization and fixed-bed reforming stages, the hydrogen concentration is higher, the temperature is higher and the space velocity is lower in the reforming stage than in the isomerization stage. When the fixed-bed reforming conditions are maintained within the ranges indicated and the charge is a C_7 to about 360° F. fraction which is substantially free of olefins and of low sulfur content, the reactor can be maintained on-stream for very long cycles, for example, for as long as 100 barrels of charge per pound of catalyst or longer, without the necessity of catalyst regeneration.

The catalyst for the fixed-bed reforming stage can be a catalyst of the type used in the hydroisomerization stage that is to say, a halogen-promoted platinum-on-alumina catalyst. However, somewhat lower halogen concentrations will be used for the reforming stage catalyst and the catalyst support can be a material other than alumina. Suitable supports or carriers other than alumina include: fresh, aged or deactivated silica-alumina composites, silica-magnesia, bauxite and the like.

In the drawing we have shown the stage in which the middle gasoline fraction is reformed in contact with a fixed-bed supported platinum catalyst as a single stage contact in a single reactor. However, as known in the art, this reforming procedure, which involves a number of different reactions results in a net temperature drop across the reactor. Advantageously, intermediate heating stages are used to maintain reaction temperature. Conventional fixed-bed platinum catalyst reforming processes employ a series of reactors, each having its own preheater to raise the temperature of the hydrocarbon stream after a drop in temperature in the preceeding reactor. Therefore, instead of the single reforming reactor **23** shown in Figure 1, our process can, as in conventional platinum catalyst hydroreforming, employ a series of reactors, a preheater being used for each reactor.

The heavy fraction in our process can have an initial boiling point from about 340 to 380° F. and an end point from about 410 to 500° F. This fraction has a considerably higher initial point than the fractions normally charged to fluid hydroreforming. However, it is a feature of our invention that the lighter hydrocarbons, other than the C_5—C_6 paraffins charged to the isomerization stage, are reformed in a fixed-bed platinum catalyst reformer and the heavy naphtha hydrocarbons are reformed in a fluid catalytic reformer employing continuous regeneration of the catalyst and a high reaction temperature. Under the reforming conditions that we use in the fluid hydroreforming stage, hydrocracking is extensive and the product has a considerably lower average molecular weight than the charge. Suitable reaction conditions for the stage in which the heavy fraction is reformed in contact with the fluidized reforming catalyst include a temperature from 850 to 980° F., a pressure from 200 to 600 p.s.i.g., a liquid-hourly space velocity from 1 to 3 vol./vol./hr. and a hydrogen concentration from 3,000 to 10,000 s.c.f./bbl. The catalyst in this stage is a finely divided supported molybdenum oxide catalyst. This type of catalyst consists of 5 to 20 weight percent molybdenum oxide deposited on activated alumina. The alumina can contain a small amount of silica, for example, about 5 percent by weight, which improves the surface characteristics of the support.

As Figure 1 shows, the product from the fluid hydroreforming stage is separated into a light and heavy fraction. The light fraction, being a high octane aromatic material, is recovered for blending to form the final gasoline product. The heavy fraction is suitable for fuel oil blending. The cut point between these two fractions can be varied somewhat but will normally be about 400° F.

Our processing system, as we have shown, includes

the treatment of olefinic gasolines such as the products of catalytic or thermal cracking. We can treat the olefinic gasoline in different ways. One procedure is shown in Figure 1 of the drawing in which we fractionate the olefinic gasoline to obtain a light fraction ranging from C_5 to 360° F. end point material, and a heavy fraction boiling from 360 to 450° F. The light olefinic fraction, which will have an octane rating from about 90 to 94 (Research, clear) is blended to form part of the final gasoline product. The heavy fraction is mixed with the heavy straight run fraction charged to the fluid catalytic hydroreforming stage. This type of reforming procedure which employs catalyst regeneration is ideally suited for reforming an olefinic gasoline which would be unsuitable as a charge stock for the non-regenerative fixed-bed platinum catalyst reforming stage.

In still another modification of our procedure for upgrading olefinic gasoline, the olefinic gasoline is separated into two fractions, a light fraction composed of C_5 and C_6 hydrocarbons, and a heavy fraction composed of the rest of the olefinic gasoline boiling up to about 450° F. The light fraction comprises a portion of the final gasoline product and the heavy fraction is passed to the fluid catalytic hydroreforming unit.

The choice of procedures for treating the olefinic gasoline will depend upon various circumstances. If the C_5—360° F. light fraction of the olefinic gasoline is of sufficiently high octane rating, for example, 85 Research, clear, or higher, it will usually be satisfactory to blend this fraction directly with the final gasoline product as shown in Figure 1. On the other hand, if the light fraction is not of sufficiently high octane rating the procedure of Figure 2 is preferable.

In the procedure of Figure 2 the olefinic gasoline is separated in column **40** into three fractions: a C_5—C_6 light fraction taken overhead via line **41**, a C_7—360° F. end point middle fraction withdrawn via line **42** and a 360—450° F. heavy fraction withdrawn via line **43**. The light fraction, which will contain C_5—C_6 olefins as well as some straight chain and branched chain C_5—C_6 paraffins, will have an octane rating from about 85 to 95 Research, clear, and is passed, after separation from light gases, directly to the final gasoline blending. The middle fraction, having an octane rating from about 85 to 90 Research, clear, can be upgraded by reforming. However, this fraction is too highly olefinic for satisfactory charging to the fixed-bed platinum catalyst reformer. Therefore, the fraction is subjected to a mild hydrogen refining pretreatment in reactor **46** in which olefins are saturated and sulfur is removed. The pretreating is in accordance with known hydrogen refining procedures and consists of contact with a fixed-bed hydrogenation catalyst in the presence of hydrogen under mild reaction conditions. Suitable catalysts include pellets or granules of molybdenum oxide on alumina, cobalt molybdate on alumina, or the like. The hydrogenating metal or metal oxide component, i.e., the molybdenum oxide or cobalt molybdate, will comprise from 5 to 20 weight percent of the catalyst composition. The alumina can contain a small amount, e.g., 5 weight percent, of silica as a stabilizer. The mild hydrorefining reaction conditions include a temperature from 600 to 750° F., a pressure from 300 to 600 p.s.i.g., a liquid-hourly space velocity from 3 to 10 vol./vol./hr. and a hydrogen-hydrocarbon ratio from 500 to 2000 s.c.f./bbl. The saturated and desulfurized product from reactor **46** is charged with the middle straight run fraction to the fixed-bed platinum catalyst reforming unit **23**. The heavy olefinic gasoline fraction is charged to the fluid catalytic hydroreforming unit **28** in admixture with the heavy straight run fraction.

Example 1 below illustrates the results that are obtainable when the process of our invention is applied to the upgrading of a debutanized 462° F. end point Kuwait straight run naphtha as defined in the following table:

INSPECTION OF KUWAIT STRAIGHT RUN NAPHTHA

Gravity, ° API	58.3
Sulfur, percent	0.155
Octane number:	
CFRR, clear	35.5
CFRR, +3 cc. TEL	60.0
Distillation, D–86:	
IBP, ° F.	96
EP, ° F.	462
10%, ° F.	154
50%, ° F.	291
90%, ° F.	430

Example 1

The naphtha is fractionated to obtain a 22.0 volume percent C_5—C_6 fraction boiling from 96 to 160° F., a 54.0 volume percent middle fraction boiling from 160 to 360° F., and a 24.0 volume percent bottoms fraction boiling from 360 to 462° F. The overhead fraction is again separated by distillation into two fractions, a 31.0 volume percent overhead fraction consisting essentially of isopentane, boiling from 80 to 90° F., and a 69.0 volume percent bottoms fraction containing n-pentane, isohexanes, and normal hexane and boiling from 90 to 160° F. The latter overhead fraction has an octane rating of 92.3 (Research, clear) (105 Research, +3 cc. TEL/gal.) and is passed to final gasoline product blending. The bottoms fraction is heated to 780° F. and then at a space velocity of 8.0 vol./vol./hr., in admixture with 500 s.c.f. of hydrogen per barrel of hydrocarbon, and at a pressure of 500 p.s.i.g. is passed through a hydroisomerization reactor containing a fixed-bed of halogen-promoted platinum-on-alumina catalyst. The reactor liquid effluent is separated from light effluent gases and the unconsumed hydrogen is recycled to the reactor. The consumption of hydrogen amounts to less than 50 s.c.f./bbl. of hydrocarbon charged. A liquid product amounting to 98.5 volume percent of the light fraction charged to the hydroisomerization reactor is recovered. This product has the following characteristics:

Hydrocarbon composition:	
Isopentane	29.5
n-Pentane	19.2
n-Hexane	10.5
Branched hexanes	33.7
Saturated cyclics	3.0
Benzene	3.6
C_7 and heavier	0.5
Gravity: ° API	86.9
Sulfur: percent	0.003
Octane number:	
CFRR, clear	82.9
CFRR, +3 cc. TEL	99.7

The middle fraction of the naphtha feed stock is mixed with hydrogen in a concentration of 7500 s.c.f./bbl. of hydrocarbon; the mixture is heated to 930° F. and at a space velocity of 3.0 vol./vol./hr. and a pressure of 500 p.s.i.g. is passed in contact with a fixed-bed of halogen-promoted platinum-on-alumina catalyst. Hydrogen is separated from the reactor effluent and is recycled to the reforming reactor feed and to the feed to the hydroisomerization stage. The net yield of hydrogen amounts to 400 s.c.f./bbl. A reformate amounting to 80.1 volume percent of the feed to the fixed-bed reformer is recovered. This product has the following characteristics:

Gravity: ° API	50.5
Sulfur: percent	0.003
Octane number:	
CFRR, clear	90.1
CFRR, +3 cc. TEL	98.8

Distillation, D–86:

IBP	° F.	118
EP	° F.	406
10%	° F.	160
50%	° F.	232
90%	° F.	338

The bottoms from the straight run naphtha fractionation is mixed with hydrogen in a concentration of 6000 s.c.f./bbl. of hydrocarbon, is preheated to a temperature of 930° F. and charged to a catalytic reactor containing a fluidized bed of molybdena-on-alumina catalyst at a space velocity of 1.2 vol./vol./hr. and a pressure of 350 p.s.i.g. The product is separated from hydrogen which is recycled. The yield of hydrogen is 330 s.c.f./bbl. The yield of liquid product is about 71 volume percent of the hydrocarbon charge to the fluid catalytic reforming reactor. The product has the following characteristics:

Gravity: ° API		45.0
Sulfur: percent		0.007
Octane number:		
CFRR, clear		94.4
CFRR, +3 cc. TEL		101.9
Distillation, D–86:		
IBP	° F.	100
EP	° F.	506
10%	° F.	144
50%	° F.	286
90%	° F.	416

This product is separated into two fractions, an 88.9 volume percent overhead fraction boiling from 97° F. and an 11.1 volume percent bottoms fraction boiling from 399° F. The light overhead fraction has the following characteristics:

Gravity: ° API		49.4
Sulfur: percent		0.009
Octane number:		
CFRR, clear		95.0
CFRR, +3 cc. TEL		101.8
Distillation, D–86:		
IBP	° F.	97
EP	° F.	398
10%	° F.	141
50%	° F.	269
90%	° F.	351

This overhead fraction from the fluid bed reformer is passed to final gasoline product blending and the bottoms fraction is passed to fuel oil blending. The final gasoline product formed by blending the straight run isopentane from the light fraction of the feed, the first stage isomerization product, the fixed-bed platinum catalyst reforming product and the light fraction of the fluid bed reforming product amounts to 80.1 volume percent of the debutanized 462° F. end point straight run naphtha and has the following characteristics:

INSPECTION OF FINAL GASOLINE PRODUCT

Gravity: ° API		61.1
Sulfur: percent		0.004
Octane number:		
CFRR, clear		89.9
CFRR, +3 cc. TEL		100.2
Distillation, D–86:		
IBP	° F.	82
EP	° F.	406
10%	° F.	114
50%	° F.	244
90%	° F.	372

Example 2 below illustrates the results that are obtainable when the process of our invention is applied to a gasoline pool comprising a 462° F. end point straight run naphtha as treated in Example 1 above and a debutanized 440° F. end point fluid catalytic cracking distillate as defined in the following table:

INSPECTION OF FCC DISTILLATE

Gravity: ° API		56.4
Sulfur: percent		0.25
Octane number:		
CFRR, clear		89.7
CFRR, +3 cc. TEL/Gal		95.6
Distillation, D–86:		
IBP	° F.	112
EP	° F.	440
10%	° F.	148
50%	° F.	278
90%	° F.	410

Example 2

The straight run naphtha is fractionated and the fractions are treated substantially in the same way as described in Example 1. The catalytically cracked olefinic distillate of the above table is separated into two fractions, an 84.6 volume percent overhead fraction boiling from 114 to 352° F. and a 15.4 volume percent bottoms fraction boiling from 365 to 457° F. The overhead olefinic fraction has the following characteristics:

Gravity: ° API		60.5
Sulfur: percent		0.16
Octane number:		
CFRR, clear		90.5
CFRR, +3 cc. TEL/Gal		96.8
Distillation, D–86:		
IBP	° F.	114
EP	° F.	352
10%	° F.	145
50%	° F.	215
90%	° F.	312

The bottoms olefinic fraction has the following characteristics:

Gravity: ° API		33.8
Sulfur: percent		0.66
Octane number:		
CFRR, clear		84.6
CFRR, +3 cc. TEL/Gal		90.9
Distillation, D–86:		
IBP	° F.	365
EP	° F.	457
10%	° F.	383
50%	° F.	392
90%	° F.	414

The overhead fraction of the FCC distillate is passed to final product blending while the bottoms fraction is blended with the 360 to 462° F. bottoms fraction of the straight run naphtha and is charged to fluid catalytic reforming under the conditions described in Example 1. The reactor effluent is separated from hydrogen which is recycled to the reactor feed. The yield of liquid reformate is about 71 volume percent of the reactor feed. The reformate is separated into two fractions, an 86.5 volume percent overhead fraction boiling from 101 to 399° F. and a 13.5 volume percent bottoms fraction boiling from 399 to 550° F. The overhead fraction of the reformate has the following characteristics:

Gravity: ° API		47.3
Sulfur: percent		0.017
Octane number:		
CFRR, clear		94.9
CFRR, +3 cc. TEL/Gal		101.4
Distillation, D–86:		
IBP	° F.	101
EP	° F.	399
10%	° F.	154
50%	° F.	288
90%	° F.	359

The bottom fraction of the reformate has a gravity of about 12.3° API and a boiling range from about 399 to 550° F.

The final gasoline product is prepared by blending the straight run isopentane separated from the straight run naphtha, the hydroisomerization product, the fixed-bed platinum catalyst reforming product, the overhead fraction of the fluid catalytic reforming product and the unconverted overhead fraction of the FCC distillate. The final gasoline product amounts to 84.7 volume percent of the total feed consisting of the straight run Kuwait naphtha and the FCC distillate and has the following characteristics:

Gravity: ° API	60.4
Sulfur: percent	0.058
Octane number:	
CFRR, clear	90.3
CFRR, +3 cc. TEL/Gal	99.0
Distillation, D–86:	
IBP ° F.	82
EP ° F.	400
10% ° F.	114
50% ° F.	241
90% ° F.	369

Example 3 below illustrates the results obtaintable when the process of our invention is applied to a gasoline pool comprising a 462° F. end point straight run naphtha as treated in Example 1 and a debutanized 449° F. end point thermally cracked gasoline as defined in the following table:

INSPECTION OF THERMALLY CRACKED GASOLINE

Gravity: ° API	54.6
Sulfur: percent	0.37
Octane number:	
CFRR, clear	79.0
CFRR, +3 cc. TEL/Gal	87.2
Distillation, D–86:	
IBP ° F.	86
EP ° F.	449
10% ° F.	148
50% ° F.	279
90% ° F.	393

Example 3

The straight run naphtha is fractionated and the fractions are treated substantially in the same way as described in Example 1. The olefinic thermally cracked gasoline of the above table is separated into three fractions, a 14.5 volume percent overhead fraction boiling from 86 to 160° F., a 65.0 volume percent middle fraction boiling from 170 to 350° F. and a 20.5 volume percent bottoms fraction boiling from 360 to 450° F. The overhead fraction of the thermally cracked gasoline has the following characteristics:

Gravity: ° API	76.9
Sulfur: percent	0.051
Octane number:	
CFRR, clear	86.3
CFRR, +3 cc. TEL/gal.	95.8
Distillation, D–86:	
IBP ° F.	86
EP ° F.	160
10% ° F.	94
50% ° F.	123
90% ° F.	153

The middle fraction of the thermally cracked gasoline has the following characteristics:

Gravity: ° API	56.9
Sulfur: percent	0.17
Octane number:	
CFRR, clear	75.8
CFRR, +3 cc. TEL/gal.	88.7
Distillation, D–86:	
IBP ° F.	170
EP ° F.	350
10% ° F.	177
50% ° F.	260
90% ° F.	332

The bottoms fraction of the olefinic thermally-cracked gasoline has the following characteristics:

Gravity: ° API	31.5
Sulfur: percent	0.15
Octane number:	
CFRR, clear	71.6
CFRR, +3 cc. TEL/gal.	83.4
Distillation, D–86:	
IBP ° F.	360
EP ° F.	450
10% ° F.	369
50% ° F.	405
90% ° F.	441

The overhead fraction, being of sufficiently high octane rating, is passed to final product blending. The middle fraction is mixed with excess recycle hydrogen from the fixed-bed platinum reforming stage in a concentration of 4000 s.c.f./bbl., the hydrocarbon-hydrogen mixture is heated to 650° F. and is passed in contact with a fixed-bed nickel-cobalt-molybdenum-on-alumina catalyst at a space velocity of 3.0 vol./vol./hr. and a pressure of 400 p.s.i.g. The product of this hydrogen treatment is separated from light gases and is blended with the middle fraction of the straight run naphtha for charging to the fixed-bed platinum catalyst reforming stage under substantially the conditions described in Example 1. The reformate from the fixed-bed reforming stage amounts to 83.4 volume percent of the feed mixture comprising the middle straight run fraction and the hydrogen treated middle fraction of the thermally cracked gasoline and has the following characteristics:

Gravity: ° API	46.5
Sulfur: percent	0.004
Octane number:	
CFRR, clear	91.6
CFRR, +3 cc. TEL/gal.	98.4
Distillation, D–86:	
IBP ° F.	118
EP ° F.	405
10% ° F.	152
50% ° F.	251
90% ° F.	362

The bottoms fraction of the thermally cracked gasoline is blended with the bottoms fraction of the straight run naphtha for charging to fluid bed reforming under substantially the conditions described in Example 1. The reactor effluent is separated from hydrogen and light gases and a liquid product yield of about 71 volume percent of the reforming feed is obtained. This product is separated into two fractions, an overhead fraction comprising 87.7 volume percent of the reformate and a bottoms fraction comprising 12.3 volume percent of the reformate. The bottoms fraction is passed to fuel oil blending. The overhead fraction is passed to final gasoline product blending. The final gasoline product, composed of the straight run isopentane, the hydroisomerization product, the fixed-bed platinum reforming product and the fluid bed reforming product amounts to 81.9 volume percent of the gasoline pool, comprising the straight run naphtha and the thermally cracked gasoline and has the following characteristics:

Gravity: ° API	57.8
Sulfur: percent	0.008

Octane number:		
CFRR, clear		90.3
CFRR, +3 cc. TEL/gal.		99.3
Distillation, D-86:		
IBP	° F.	83
EP	° F.	401
10%	° F.	115
50%	° F.	240
90%	° F.	370

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A process for increasing the octane rating of gasoline which comprises fractionating a full range straight run gasoline to obtain a light paraffinic fraction consisting essentially of C_5 and C_6 paraffins, a middle fraction having an end point from about 320° to about 360° F. and a heavy residual fraction of about 450° F. end point, increasing the octane rating of said light fraction in a hydroisomerization stage comprising contacting straight chain C_5 and C_6 paraffins in admixture with hydrogen with a fixed-bed, halogen-promoted, platinum-on-alumina catalyst under hydroisomerization conditions including a hydrogen concentration from about 50 to 1,000 s.c.f./bbl. of hydrocarbon, a liquid-hourly space velocity greater than 5 vol./vol./hr. and a temperature from 600° to 850° F. and recovering a product of substantially the same average molecular weight as said light fraction and higher branched chain paraffin content, increasing the octane rating of said middle fraction in a fixed-bed catalytic reforming stage comprising contacting said middle fraction in admixture with hydrogen with a fixed-bed, halogen-promoted, platinum-on-alumina catalyst under reforming conditions including a hydrogen concentration from 3,000 to 10,000 s.c.f./bbl., a liquid-hourly space velocity from 1 to 4 vol./vol./hr. and a temperature from 850° to 950° F., separating light gases from the reactor effluent of said fixed-bed catalytic reforming stage and obtaining a normally liquid product entirely of the gasoline boiling range and of higher aromatic content and octane rating than said middle fraction, treating said heavy fraction in a fluid catalytic reforming stage wherein said heavy fraction in admixture with hydrogen is contacted with a fluidized supported molybdenum oxide catalyst under reforming conditions including a hydrogen concentration from 3,000 to 10,000 s.c.f./bbl., a space velocity from 1 to 3 vol./vol./hr., and a temperature from 850 to 980° F., recovering a conversion product of substantially lower average molecular weight and higher aromatic content than said heavy fraction, fractionating said product to recover a light fraction and a residual fraction, and blending said light fraction with the entire normally liquid hydrocarbon products of said hydroisomerization stage and said fixed-bed catalytic reforming stage to obtain a gasoline product having an octane rating of at least about 90 Research, clear.

2. A process for increasing the octane rating of a refinery gasoline pool including straight run and olefinic gasoline which comprises fractionating a full range straight run gasoline fraction to obtain a light paraffinic fraction consisting essentially of C_5 and C_6 paraffins, a C_7 to about 360° F. middle fraction and a heavy fraction boiling from about 360 to 450° F., fractionating a full range olefinic gasoline to obtain a light fraction comprising C_5 and C_6 hydrocarbons and a heavier fraction, increasing the octane rating of said light straight run fraction in a hydroisomerization stage by contacting n-pentane and n-hexane in admixture with hydrogen with a fixed-bed, halogen-promoted, platinum-on-alumina catalyst under hydroisomerization conditions including a hydrogen concentration from about 50 to 1,000 s.c.f./bbl. of hydrocarbon, a liquid-hourly space velocity greater than 5 vol./vol./hr. and a temperature from 600 to 850° F. and recovering a product of substantially the same average molecular weight as said light straight run fraction and of higher branched chain paraffin content, increasing the octane rating of said middle fraction in a fixed-bed catalytic reforming stage by contacting said middle fraction in admixture with hydrogen with a fixed-bed, halogen-promoted, platinum-on-alumina catalyst under reforming conditions including a hydrogen concentration from 3,000 to 10,000 s.c.f./bbl., a liquid-hourly space velocity from 1 to 4 vol./vol./hr. and a temperature from 850° to 950° F. and recovering from said fixed-bed catalytic reforming stage a normally liquid product entirely of the gasoline boiling range and of higher aromatic content and octane rating than said middle fraction, mixing said heavy olefinic fraction with said heavy straight run fraction and treating the resulting combined fraction in a fluid catalytic reforming stage wherein the combined heavy fraction in admixture with hydrogen is contacted with a fluidized supported molybdenum oxide catalyst under reforming conditions including a hydrogen concentration from 3,000 to 10,000 s.c.f./bbl., a liquid-hourly space velocity from 1 to 3 vol./vol./hr. and a temperature from 850 to 980° F., recovering a conversion product of substantially lower average molecular weight and of higher aromatic content than the combined heavy fraction, fractionating said product to recover a light fraction and a residual fraction, and blending said light fraction with the light fraction of said olefinic gasoline and with the entire normally liquid hydrocarbon products of said hydroisomerization stage and said fixed-bed catalytic reforming stage to obtain a gasoline product having an octane rating of at least about 90 Research, clear.

3. A process in accordance with claim 2 in which said full range olefinic gasoline is fractionated to obtain a C_5 to 360° F. light fraction and a 360° to 450° F. heavy fraction.

4. A process according to claim 2 in which said full range olefinic gasoline is fractionated to obtain a light fraction consisting essentially of C_5 and C_6 hydrocarbons and a C_7 to 360° F. middle fraction, said middle fraction being passed in admixture with hydrogen to a saturating and desulfurizing pretreatment comprising contact with a fixed-bed hydrogenating catalyst at a temperature from 600° to 750° F., a liquid-hourly space velocity from 3 to 10 vol./vol./hr. and a hydrogen concentration from 500 to 2,000 s.c.f./bbl., said pretreated fraction being mixed with the straight run middle fraction charged to said fixed-bed platinum catalyst reforming stage.

5. A process according to claim 2 in which said full range olefinic gasoline is fractionated to obtain a light fraction consisting essentially of C_5 and C_6 hydrocarbons and a heavy fraction consisting essentially of C_7 and higher hydrocarbons.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,944,959 July 12, 1960

Robert E. Kline et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 9, line 71, for "°F-- 372" read -- °F-- 375 --.

Signed and sealed this 10th day of January 1961.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents