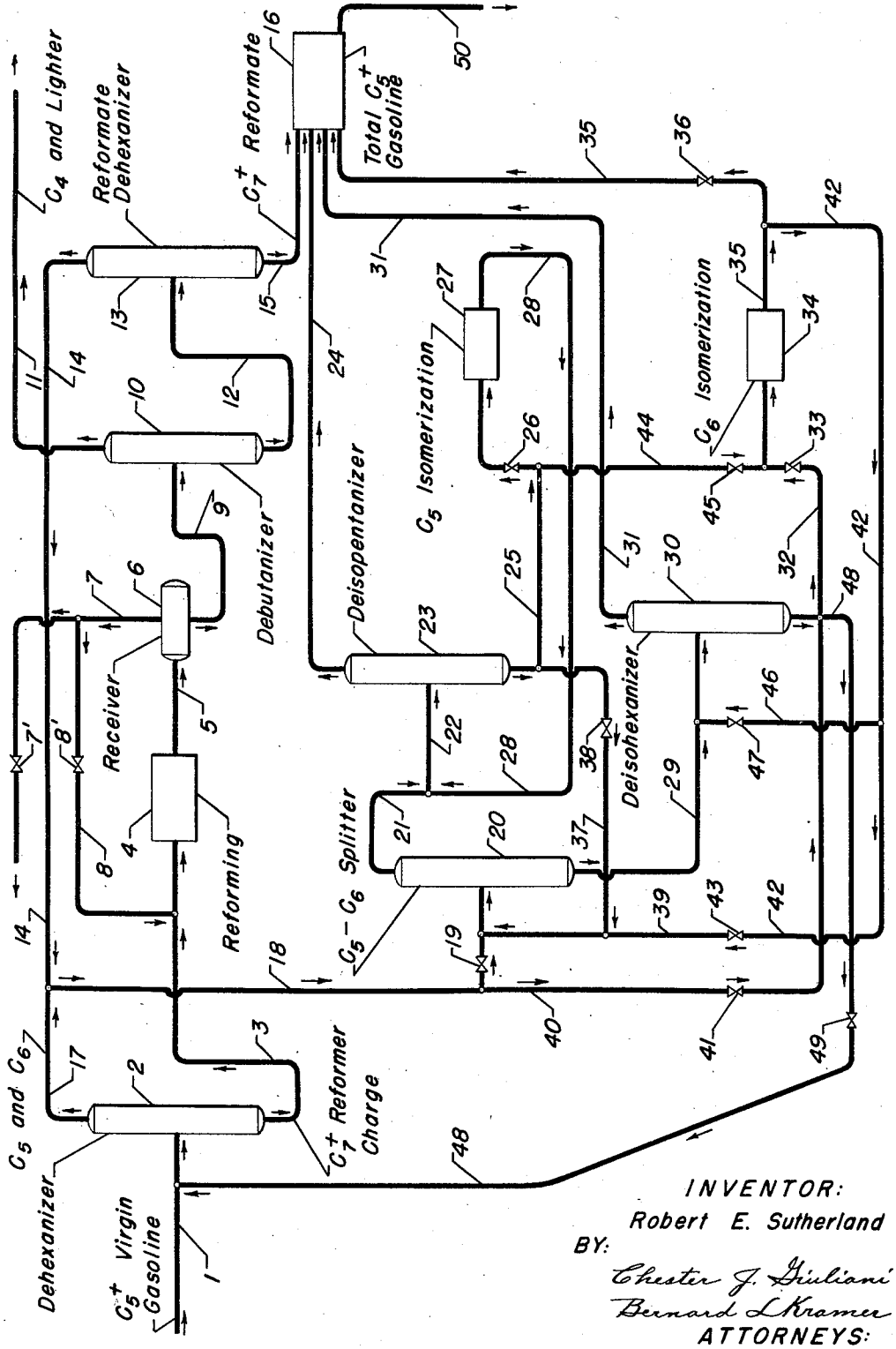
Sept. 22, 1959 R. E. SUTHERLAND 2,905,619

UPGRADING GASOLINE

Filed June 28, 1956



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United States Patent Office 2,905,619
Patented Sept. 22, 1959

2,905,619

UPGRADING GASOLINE

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Application June 28, 1956, Serial No. 594,592

3 Claims. (Cl. 208—64)

This invention relates to a novel process for upgrading gasoline and more particularly to an integrated process in which a gasoline is separated into selected fractions and the selected fractions are subjected to independent and selected conditions to produce a final product of high octane value.

In order to provide the public with more powerful motor vehicles, the automobile industry is manufacturing engines of greater horsepower and accordingly higher compression ratios. These engines require gasolines of higher octane value in order to operate satisfactorily therein. This, in turn, challenges the petroleum industry to produce gasolines of even higher octane values than the high octane gasolines presently being produced. The present invention provides a novel combination process of mutually related and interdependent steps whereby gasoline is upgraded to these higher octane values.

In accordance with the present invention, a gasoline is fractionated to separate a C_6 and lighter fraction and a C_7 and heavier fraction. The C_7 and heavier fraction is subjected to catalytic reforming to upgrade this fraction of the gasoline. The reformed products are fractionated to separate a C_6 and lighter fraction, which fraction is combined with the previously separated C_6 and lighter fraction, and the mixture is subjected to isomerization to convert the low octane normal paraffins into high octane branched paraffins. The isomerized products are combined with the reformed products to form a final product of high octane value.

Catalytic reforming of gasoline serves to considerably improve its octane value. However, the pentanes contained in the gasoline fraction undergo only minor conversion when subjected to reforming in admixture with the higher boiling gasoline components. Therefore, it generally is preferred to separate the pentanes from the gasoline charge and to blend the separated pentanes with the reformed gasoline products. However, the pentanes, as well as the hexanes, contain normal paraffins of low octane number and these paraffins lower the overall octane value of the final product. In accordance with the present invention, the pentanes and hexanes are fractionated to separate the high octane paraffins from the low octane paraffins, and the latter are isomerized into high octane branched chain paraffins. The high octane paraffins then are blended with the reformed gasoline fraction to produce a final blend of high octane value.

As an illustration of the above, isopentane has a Research octane value, when leaded with 3 cc. of tetraethyl lead, of 103.5. On the other hand, normal pentane has a leaded octane number of only 85. It is readily seen that the presence of the low octane normal pentane in the final gasoline blend reduces the overall octane number of the gasoline. Similarly, normal hexane has a leaded octane number of only 65.3, whereas the branched chain hexanes have leaded octane numbers in excess of 93. Here again, the presence of normal hexane in the final product considerably reduces the overall octane number of the gasoline. In accordance with the present invention, these low octane components are converted into high octane products and, when blended in the final gasoline, serve to produce a final gasoline of considerably higher octane number than previously attained.

From the heretofore description, it will be noted that the present invention provides an integrated combination of isomerization and catalytic reforming for the production of high octane gasoline. The high octane product cannot be achieved by catalytic reforming alone, except by using extremely severe operating conditions which, in turn, results in excessive losses in yield, as well as in low catalyst life. These excessive losses and low catalyst life prohibit any practical or commercial utilization of the catalytic reforming process in this manner for obvious economic reasons.

It will be noted that the novel process of the present invention selectively separates the low octane components and independently converts them into high octane components. By separating these low octane components and subjecting them to conversion under optimum conditions, improved results are obtained. These improved results include higher overall yields of high octane gasoline, operation of the catalytic reforming at less severe conditions than otherwise would be required, with the concomitant high yields and long catalyst life in the reforming step of the process, the greater flexibility in operation to permit the processing of a variety of gasoline charge stocks, as well as producing gasolines of even higher octane numbers as may be required to meet market demands of the future. Furthermore, by the novel method of the present invention, the low octane components are converted in the absence of the high octane components, and therefore any possible undesired conversion of the high octane components is avoided.

The invention is further explained with reference to the accompanying diagrammatic flow drawing which illustrates several specific embodiments thereof. It is understood that the drawing is presented for illustrative purposes and that the scope of the invention is not limited to the specific embodiments illustrated therein.

In the interest of simplicity, the drawing will be described with reference to the particularly preferred embodiment of the invention, to be followed with a description of the alternative, but not necessarily equivalent, embodiments of the invention. The gasoline charge is introduced to the process through line 1 and is directed into dehexanizer 2. In the preferred embodiment, the gasoline charge has a boiling range of from C_5 to about 400° F., although the end point may be higher, ranging up to about 450° F. The gasoline charge preferably is a saturated gasoline and thus may comprise straight run gasoline, natural gasoline, etc., or hydrogenated unsaturated gasolines, such as cracked gasoline, coker distillate, etc., which previously had been subjected to desulfurization-hydrogenation, or a mixture of these gasolines.

In accordance with the present invention, the gasoline charge is fractionated in dehexanizer 2 to separate an overhead fraction comprising pentanes and hexanes, and a bottoms fraction comprising heptanes and higher boiling components, the latter being referred to as C_7 and heavier fraction. The C_7 and heavier fraction is withdrawn from dehexanizer 2 through line 3 and is subjected to reforming in reforming zone 4.

While reforming zone 4 is illustrated as a single zone, it is understood that this system will comprise heaters, heat exchangers, a series of reaction zones, generally 3 or 4, coolers and receivers. The reforming is effected at a temperature of from about 800° to about 1050° F., at a pressure of from about 100 to about 1000 pounds or more per square inch, a liquid hourly space velocity of from about 0.5 to 10, and in the presence of hydrogen in a mol ratio to hydrocarbon of from about 0.5 to 20.

Any suitable reforming catalyst may be utilized and preferably comprises a composite of alumina and platinum, the platinum being in a concentration of from about 0.01 to about 5% by weight of the catalyst, and more particularly a composite of alumina, platinum and combined halogen, the platinum being in a concentration of from about 0.01 to about 3% and the halogen being in a concentration of from about 0.2 to about 3% by weight of the final catalyst. A particularly preferred catalyst comprises a composite of alumina, platinum in a concentration of from about 0.2 to about 1% by weight and combined halogen in a concentration of from about 0.2 to about 1% by weight of the final catalyst. The halogen preferably comprises fluorine and/or chlorine. Other platinum-containing catalysts comprise composites of platinum-silica, platinum-silica-alumina, platinum-silica-zirconia, platinum-silica-alumina-zirconia, platinum-silica-thoria, platinum-silica-alumina-thoria, platinum-silica-magnesia, platinum-silica-alumina-magnesia, etc. The catalyst may be in the form of powder or larger size granules of irregular size and shape, but preferably is in the form of particles of uniform size and shape as obtained by pilling, extruding, the oil drop method, etc. The reforming process produces hydrogen and, in a preferred embodiment of the invention, the hydrogen is recycled within the system.

The reformed products are withdrawn from zone **4** through line **5** and are directed to receiver **6**. In receiver **6**, hydrogen-containing gas is withdrawn through line **7**, and while all or a portion may be removed from the process through valve **7'**, at least a portion of the hydrogen is recycled by way of line **8**, valve **8'**, and line **3** within the system for further use therein.

The reformed gasoline product is directed from receiver **6** through line **9** into debutanizer **10**. In this zone, butanes and lighter products are separated and are withdrawn therefrom through line **11** for further treatment or use as desired. The liquid products are withdrawn from zone **10** through line **12** and are directed to dehexanizer **13**. In dehexanizer **13** the C_5 and C_6 hydrocarbons are separated and are withdrawn therefrom through line **14** for further conversion in the manner to be set forth hereinafter. The C_7 and heavier reformed products are withdrawn from zone **13** through line **15** and, in the preferred embodiment of the invention, are directed into gasoline blending zone **16**.

The C_5 and C_6 hydrocarbons separated in zone **2** are withdrawn therefrom through line **17** and are commingled with the C_5 and C_6 hydrocarbons withdrawn from zone **13** and directed through line **14**, the mixture then being directed by way of line **18** and valve **19** to splitter **20**. Splitter **20** functions to separate an overhead fraction comprising pentanes and a lower fraction comprising hexanes.

The pentanes separated in zone **20** are withdrawn therefrom through line **21** and are directed through line **22** to deisopentanizer **23**. The deisopentanizer functions to split an overhead fraction comprising isopentane from a bottoms fraction comprising normal pentane. It will be noted that zone **23** functions to separate the isopentane originally contained in the gasoline charge, as well as the isopentane contained in the reformed products. The isopentane separated in zone **23** is withdrawn therefrom through line **24** and, in a preferred embodiment of the invention, at least a portion thereof is directed to gasoline blending zone **16**. Isopentane has a leaded Research octane number of about 103 and thus comprises a desirable component for the final gasoline blend.

Normal pentane has a leaded Research octane number of about 85 and, in order to produce the super gasolines of the present invention, is of too low an octane number to be included in any substantial quantities in the final gasoline blend. In accordance with the present invention, the normal pentane fraction is withdrawn from deisopentanizer **23** through line **25** and is directed through valve **26** into pentane isomerization zone **27**.

Isomerization zone **27** likewise comprises suitable heater, heat exchanger, reactor, cooler, etc. In a preferred embodiment of the invention, only one reactor will be required because the overall heat of reaction is low. Any suitable isomerization catalyst may be utilized in zone **27**. A preferred catalyst comprises a platinum-containing composite and still more particularly the alumina-platinum-combined halogen catalyst described above for use in the reforming zone. With these catalysts, isomerization of pentane generally is effected at a temperature of from about 700 to about 950° F. and preferably of from about 750° to about 850° F., at a pressure of from about 50 to about 1000 pounds or more per square inch, and more particularly of from about 100 to about 500 pounds per square inch, a liquid hourly space velocity of from about 0.5 to 5 and a hydrogen to hydrocarbon ratio of from about 0.5 to about 5. In the isomerization reaction, the consumption or production of hydrogen is of very low order and the hydrogen preferably is recycled within the isomerization system by well-known means, not illustrated, or it may be supplied, either continuously or intermittently, from the reforming system.

The isomerized pentane fraction is withdrawn from zone **27** through line **28** and it is returned by way of line **22** to deisopentanizer **23**. Thus, the deisopentanizer serves to separate the isopentane formed in zone **27**, as well as the isopentane contained in the original gasoline charge and that produced in the reforming reaction. As hereinbefore set forth, the isopentane is directed through line **24** into gasoline blending zone **16**. Normal pentane is withdrawn from the lower portion of zone **23** through line **25** and is recycled in zone **27** for isomerization therein.

While a platinum-containing catalyst as hereinbefore described is preferred for use in zone **27**, it is understood that other suitable isomerization catalysts may be employed. The other isomerization catalysts include aluminum chloride, aluminum bromide, zinc chloride, etc., along with the corresponding hydrogen halide. In one embodiment, the metal halide catalysts are composited with a suitable carrier such as alumina, bauxite, clay, etc., and utilized as a fixed bed of catalyst in the reaction zone. However, it is understood that these catalysts may be utilized in liquid form. When utilizing these catalysts, the isomerization reaction generally is effected at a temperature of from about 150° to about 300° F. It is understood that the various isomerization catalysts are not necessarily equivalent and that the preferred catalyst comprises the platinum-containing catalyst hereinbefore described.

Regardless of the particular isomerization system employed, operating conditions are selected so that the isomerization reaction will be selective, with a minimum of cracking or other side reactions. By separately subjecting the pentane fraction to isomerization in an independent zone under optimum conditions for this reaction, and with the recycle operation illustrated, substantially complete isomerization of the normal pentane to isopentane may be effected in the present process. As hereinbefore set forth, this serves to reduce the amount of normal pentane in the final gasoline product to a minimum. In contrast thereto, it has been found that the inclusion of the pentanes in the gasoline charge to reforming effects very little isomerization of the normal pentanes to isopentanes.

The hexanes separated in splitter **20** are withdrawn therefrom through line **29** and are directed to deisohexanizer **30**. In deisohexanizer **30**, low octane normal hexane is separated as a bottoms product from lower boiling higher octane branched chain hexanes. The branched chain hexanes are withdrawn through line **31**

and, in the preferred embodiment of the invention, at least a portion thereof is directed to gasoline blending zone **16**. Here again, it will be noted that the deisohexanizer serves to separate the lower boiling higher octane branched chain hexanes originally present in the gasoline charge to the process, as well as that produced in the reforming step of the process.

The normal hexane and higher boiling C_6 components are withdrawn from zone **30** through line **32** and are directed through valve **33** to isomerization zone **34**. In zone **34**, the hexanes are subjected to isomerization under optimum conditions which are independently controlled to obtain maximum conversion. This isomerization zone will be similar to that hereinbefore described in connection with the pentane isomerization, and may utilize the same type of catalyst hereinbefore described. Here again, it is preferred that the catalyst comprises the platinum-containing composite hereinbefore described. However, the conditions in this zone, while being within the range hereinbefore described, will be selected to effect maximum conversion to the desired products.

In a preferred embodiment of the invention, the isomerization products from zone **34** are withdrawn from line **35** and are directed through valve **36** to gasoline blending zone **16**. Depending upon the particular gasoline charged to the process, the isomerized product from zone **34** will contain cyclic compounds including methyl cyclopentane, cyclohexane, benzene, etc., in small but varying concentrations. These cyclic compounds are of high octane value and, in the preferred embodiment of the invention, are included in the final gasoline product of the process. The features of once through operation of the reforming, recycle operation in the pentane isomerization and once through hexane isomerization all combine to produce a final gasoline product of high octane number, without the necessity of utilizing complicated and expensive equipment and processes to separate the different type compounds present in the effluent products from these zones.

From the above description, it will be noted that the final gasoline blend comprises reformed gasoline, isopentane, low boiling high octane branched chain hexanes and isomerized hexanes. As another advantage of the process of the present invention, the gasoline blend is of low vapor pressure and therefore will permit the introduction of butanes and additional isopentanes to raise the vapor pressure to the desired 10 pounds R.V.P. or thereabouts. The introduction of these materials further increases the octane rating of the final gasoline product. Depending upon the particular charge, the final gasoline blend will have a leaded Research octane number of above 95 and may range up to 102 or even higher. Of equal importance is the fact that the integrated process of the present invention produces a total pool gasoline in a yield of from 6 to 10% or more greater than obtainable by prior methods. It is apparent that this increase in yield of high octane gasoline is of extreme importance from a commercial consideration.

In conventional fractionation, a small amount of hexanes will be carried over in the overhead fraction from splitter **20** and will accumulate in the bottoms fraction in deisopentanizer **23**. In order to avoid the buildup of the hexanes in this step of the process, a drag stream of the bottoms fraction is continuously or intermittently directed through line **27** and valve **38** to be returned by way of lines **39** and **19** to splitter **20**. In this manner, the hexanes will be removed from the C_5 fraction and will not build up in the pentane isomerization system.

The process flow hereinbefore described comprises the particularly preferred method of operation. The drawing also illustrates several alternative, but not necessarily equivalent, operations which may be utilized within the broad scope of the present invention. While it is preferred to separately isomerize the C_5 fraction and the C_6 fraction, in some cases it may be satisfactory to effect the isomerization of the C_5's and C_6's in a single isomerization zone. In this embodiment, the pentanes and hexanes may be directed through line **18**, line **40**, valve **41**, line **32** and line **33** to isomerization zone **34**. While the isomerization products may be directed through line **35** and valve **36** to gasoline blending zone **16**, in another embodiment the isomerization products are directed through line **42**, valve **43** and line **19** to splitter **20**. Here again, the splitter serves to separate pentanes from hexanes and the former is directed to deisopentanizer **23**, while the latter is directed to deisohexanizer **30**. The bottoms fraction from both of these fractionators are returned to the isomerization zone. This is accomplished by passing the bottoms from zone **23** through line **25**, line **44**, valve **45** and line **32** to zone **34**, and passing the bottoms fraction from zone **30** through line **32** and valve **33** to zone **34**. As hereinbefore set forth, the use of a single isomerization zone for converting both the pentanes and hexanes generally is not as desirable as employing separate zones for these isomerizations. However, in some cases, the octane value of the final gasoline will be sufficient to meet prevailing market requirements and therefore the use of a single isomerization zone may be satisfactory.

In another embodiment of the invention when utilizing a single isomerization zone, the pentane-hexane fraction being directed through line **18** is passed through valve **19** into zone **20**, and subjected to separation therein as well as in deisopentanizer **23** and deisohexanizer **30**. However, the normal pentane is directed through lines **25**, **44** and **32** to isomerization zone **34**, instead of being subjected to separate isomerization as in the particularly preferred embodiment of the invention.

In still another embodiment, when employing a separate isomerization zone each for the pentane and hexanes, and recycling of the hexanes is utilized, the effluent isomerization products from zone **34** are directed through lines **35**, **42** and **46**, valve **47** and line **29** and deisohexanizer **30** for separation of the low boiling high octane branched chain hexanes from normal hexane, the latter to be recycled by way of line **32** to zone **34** for further isomerization.

When utilizing recycle type operation of the isomerized hexanes, there may be a buildup of heptanes in deisohexanizer **30**. This is similar to the possible buildup of hexanes in deisopentanizer **23** heretofore described. In order to prevent the buildup of heptanes in zone **30**, a drag stream is directed by way of line **48**, valve **49** and line **1** to dehexanizer **2**. In dehexanizer **2** the heptanes will be concentrated in the bottoms fraction and subjected to reforming as part of the charge thereto. The hexanes will be recycled to isomerizer **34** by the circuit heretofore described.

When utilizing recycle type operation of the hexane isomerization products, there is a possibility of the presence of cyclic compounds which may interfere with fractionation in zone **30** and possibly in zones **20** and **23**. It is within the scope of the present invention to remove the cyclic compounds in any suitable manner, not illustrated, as for example by subjecting the isomerized products to extraction with a solvent which selectively removes the cyclic compounds and particularly the aromatics. As hereinbefore set forth, the necessity for such treatment is avoided in the particularly preferred embodiment of the invention in which the isomerized products from zone **34** are supplied directly to gasoline blending zone **16**.

Although not illustrated in the drawing, in another embodiment of the invention, additional fractionating zones may be provided to split the heptanes into high octane low boiling components and low octane high boiling components and the separated high boiling heptane fraction may be subjected to isomerization in the

same or different zone or zones from that used for isomerizing the pentanes and/or hexanes. In this embodiment, fractionating zones 2 and 13 will function to separate C_5, C_6 and C_7 from C_8 and heavier components. The pentanes will be separated from the hexanes and heptanes in one zone, and the hexanes will be separated from the heptanes in a separate fractionation zone. These separate fractions then may be subjected to further fractionation to separate the low boiling high octane fractions from the normal higher boiling fractions. In this embodiment, the charge to the reforming zone will comprise C_8 and heavier.

In the interest of simplicity, heaters, heat exchangers, coolers, condensers, pumps, receivers and similar appurtenances have been omitted from the drawing. These details are well-known in the art and are not required for understanding the present invention. Similarly, details of the internals of the fractionating zones have been omitted, it being understood that any suitable trays, side-to-side pans, bubble decks, etc. will be employed to obtain separation of the charge and intermediate fractions into the desired components.

As hereinbefore set forth, the novel process of the present invention produces a high yield of high octane gasoline product, which product is withdrawn from the process through line 50. The final gasoline product will have a Research leaded octane number above 95 and up to 102 or more. Another advantage to the process of the present invention is that the severity of the reforming operation is lower than otherwise would be required to reach this high octane product in the absence of the isomerization steps of the process Therefore, the yield obtained in the reforming operation is considerably increased and the life of the reforming catalyst is considerably extended. Of utmost importance is the fact that the process of the present invention produces this high octane gasoline product with an increase in yield of 6 to 10% or more, over and above that previously attainable.

The following examples are introduced to illustrate further the novelty and utility of the present invention but not with the intention of unduly limiting the same.

Example I

This example illustrates the advantages of the present invention when processing Arabian straight run gasoline having a boiling range of from 204° to 362° F., an API gravity of 57.9° and a Research clear octane number of 34. The octane number of the total gasoline product to be obtained is 98 Research leaded.

On the basis of charging 10,000 barrels per day, the gasoline is split into 2,200 barrels per day of C_5 and C_6 and 7,800 barrels per day of C_7 and heavier. The C_5 and C_6 fraction is further split into 1,100 barrels per day each of a C_5 fraction and of a C_6 fraction.

The C_7 and heavier fraction is subjected to reforming in the presence of a catalyst comprising alumina, about 0.4% by weight of platinum and about 0.5% by weight of combined halogen, the latter comprising about 0.3% by weight of combined fluorine and about 0.2% by weight of combined chlorine. The reforming is effected in a series of 3 catalyst-containing reactors with intervening heating of the reactor effluents between reactors. The charge to reforming is introduced into the reaction zone at a temperature of about 895° F., and at a space velocity of about 2.5. The reactors are maintained at a pressure of about 500 pounds per square inch, and hydrogen is recycled to maintain a hydrogen to hydrocarbon ratio of 8:1. Other portions of the same catalyst are used in the pentane isomerization and hexane isomerization zones. The pentane isomerization is effected at a temperature of 785° F., a pressure of 310 pounds per square inch, while utilizing a hydrogen to hydrocarbon ratio of 1:1. The hexane isomerization is effected at a temperature of 760° F., a pressure of 310 pounds per square inch, while utilizing a hydrogen to hydrocarbon ratio of 3:1.

From the above operation, there is produced a total C_5 and heavier gasoline product of 8,400 barrels per day, which is an overall yield of 84%, based on the original gasoline charge. In contrast, in an operation in which catalytic reforming alone is used and is increased in severity to produce a 98 leaded octane number product, the overall yield is 7,410 barrels per day or 74.1%, based on the original gasoline charge. It will be noted that 990 barrels per day of additional gasoline product is produced through the use of the process of the present invention.

Example II

In an operation similar to that described in Example I but utilizing a Wyoming straight run gasoline charge and operating to produce a leaded Research octane product of 97, operation in accordance with the present invention yields 1,010 additional barrels per day of 97 octane gasoline as compared to catalytic reforming alone at a severity necessary to achieve this octane product. The Wyoming straight run gasoline has a boiling range of 210 to 400° F., an API gravity of 56.4° and a Research clear octane number of 52.5. It is split into 1,560 barrels per day of a pentane fraction, 1,920 barrels per day of a hexane fraction and 6,520 barrels per day of a C_7 and heavier fraction. Each fraction is processed in a manner similar to that described in Example I.

I claim as my invention:

1. A process for producing high octane number motor fuel from low octane number gasoline which comprises fractionating said gasoline to separate therefrom a C_5–C_6 fraction and a heavier fraction, reforming said heavier fraction and separating from the resultant products a C_5–C_6 fraction and a reformed gasoline fraction, combining said C_5–C_6 fractions and spliting the resultant mixture into a C_5 fraction and a C_6 fraction, separately fractionating said C_5 fraction and said C_6 fraction to separate isopentane from normal pentane and branched chain hexanes from normal hexane, subjecting the thus separated normal pentane and normal hexane to catalytic isomerization, commingling resultant isomerized products with portions, at least, of said reformed gasoline fraction, said isopentane and said branched chain hexanes, and recovering the resultant blend as said high octane number motor fuel.

2. The process of claim 1 further characterized in that said normal pentane and said normal hexane are isomerized in admixture.

3. The process of claim 1 further characterized in that said normal pentane and said normal hexane are separately isomerized.

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