Feb. 7, 1961 A. CLARK 2,970,955

PROCESS FOR UPGRADING A PENTANE-CONTAINING NATURAL GASOLINE BY ISOMERIZATION AND REFORMING

Filed Nov. 25, 1955 2 Sheets-Sheet 1

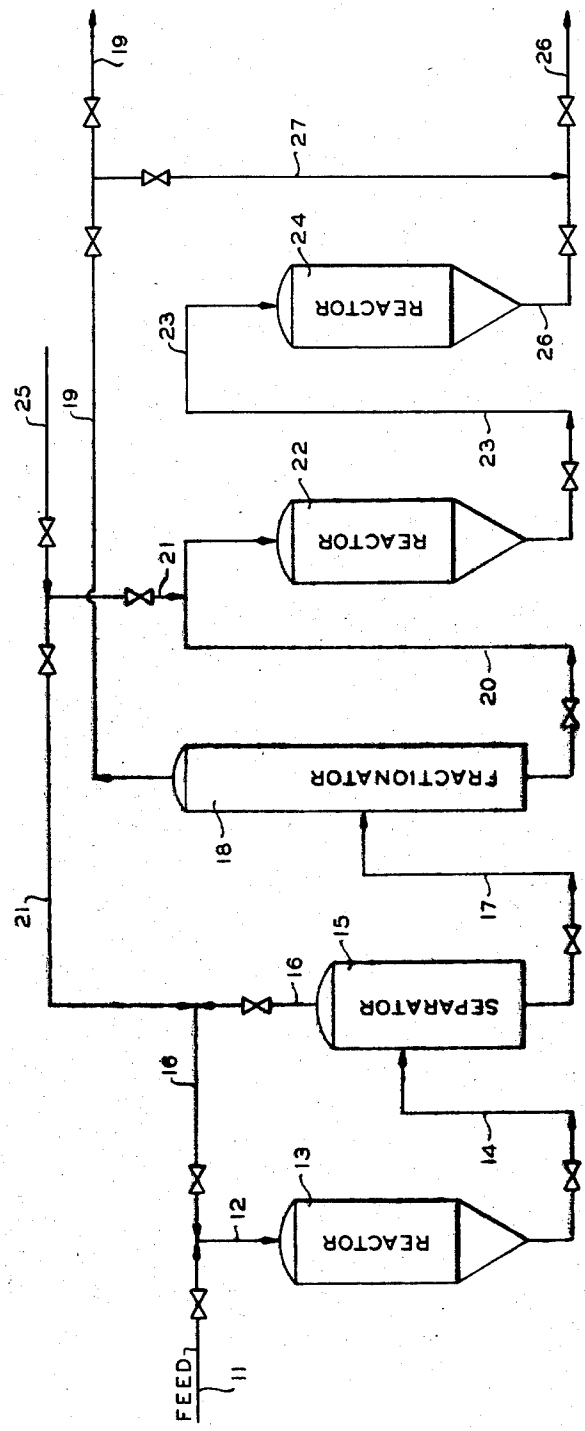


FIG. 1.

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Filed Nov. 25, 1955 2 Sheets-Sheet 2

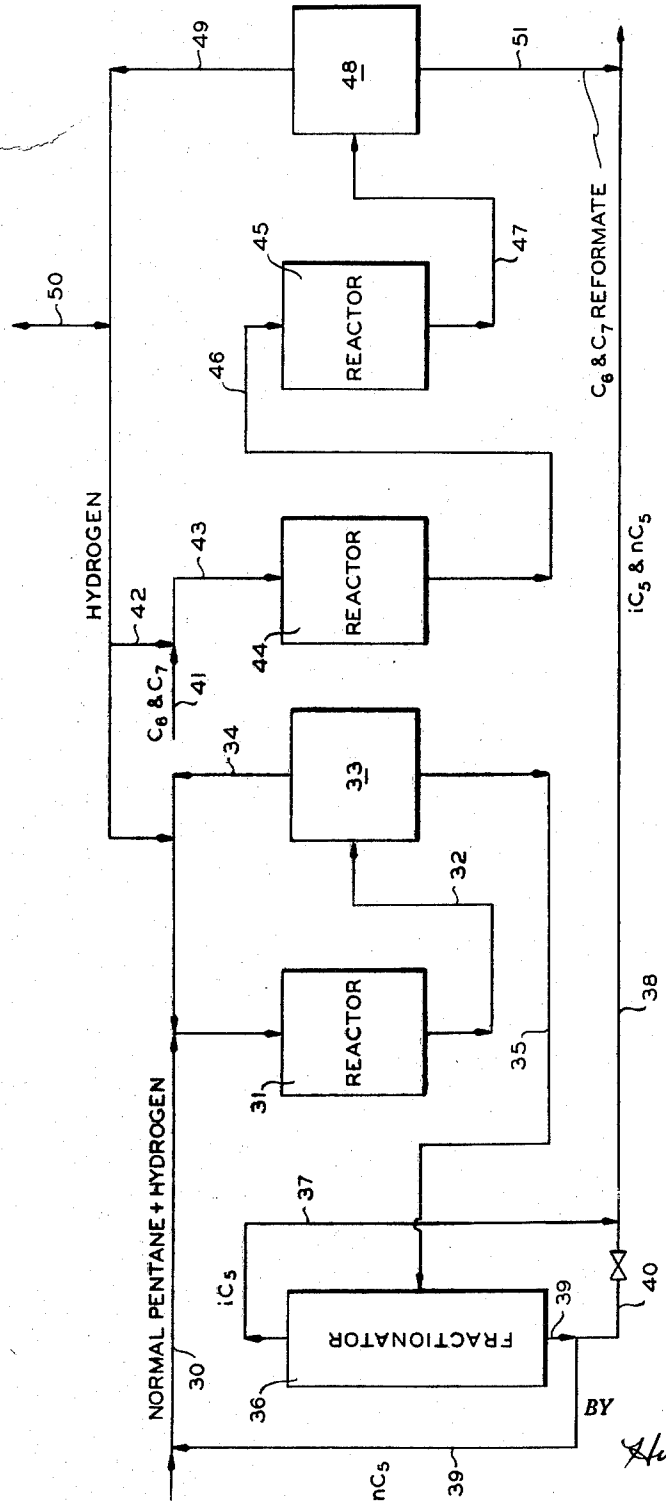


FIG. 2.

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2,970,955

PROCESS FOR UPGRADING A PENTANE-CONTAINING NATURAL GASOLINE BY ISOMERIZATION AND REFORMING

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16 Claims. (Cl. 208—65)

This invention relates to the catalytic treatment of a natural or straight-run gasoline or a component thereof. In one of its aspects the invention is concerned with a multi-stage reforming process in which isopentane or a fraction, say, an isopentane containing fraction, such as a straight-run gasoline or a C_6–C_7 fraction from such a gasoline is catalytically isomerized, and isopentane or a fraction containing the same is removed from the catalytically isomerized gasoline, following which the remaining gasoline is further catalytically treated, or reformed, obtaining, upon the combination of said fraction and said further treated gasoline, a product of improved characteristics.

Thus, it is among the objects of this invention to provide an improved gasoline product from a natural or straight-run gasoline or a component thereof; to provide said improved gasoline by advantageous combination of a series of steps in a process for the treatment of a natural or straight-run gasoline or a component thereof in presence of a catalyst in said steps; and to accomplish a higher octane value product by obtaining during the processing of said natural or straight-run gasoline, or its component, as defined herein, of at least one fraction having a desirable blending value; a more specific object being the recovery of higher yields of isopentane in a final product gasoline. Other objects, aspects, and advantages of the invention are apparent from a study of this disclosure, drawing and the appended claims.

The term "reforming" is well known in the petroleum industry and refers to the treatment of gasoline or fractions thereof to improve their anti-knock characteristics. The reforming process involves many reactions not all of which are entirely understood or even known. The primary known reactions comprise controlled or selective cracking and aromatization, the latter including dehydrogenation of C_6 naphthenic hydrocarbons to aromatics and the cyclization of straight chain or mildly branched chain aliphatic hydrocarbons of at least six carbon atoms to form aromatics. Other reactions occurring during reforming include isomerization, both of aliphatic hydrocarbons and of naphthenic hydrocarbons containing 5 and 6 carbon atoms in the ring; hydrogen transfer reactions, alkyl transfer reactions; etc.

According to the invention a natural gasoline, or a component thereof, or the like, is subjected to conditions favoring paraffin isomerization reactions, thus providing for the formation of improved yields of isopentane at least some of which, then, is removed; remaining gasoline or remaining gasoline component is then subjected to reforming under conventional reforming conditions, resulting in an improved operation because of better yields of desired products from each of the reactions; and finally, when desired, an improved product is obtained by blending isopentane with the remaining gasoline after it has been reformed.

This invention in one of its forms accomplishes the reforming of natural gasoline in the presence of hydrogen and a platinum-containing catalyst.

Also, according to this invention, there is provided a process which comprises separating a natural gasoline charging stock into at least two fractions and processing each fraction under particular conditions of operation especially suitable for that material, as later described, to obtain an improved final product.

Usually, the natural gasoline has been debutanized, as well as deisopentanized, but will contain normal pentane in substantial proportions. Also, C_8 and heavier hydrocarbons have been removed to deoil the gasoline. Thus, in one embodiment, the present invention relates to a process for reforming natural gasoline which comprises subjecting this gasoline after it has been debutanized, deisopentanized and deoiled, to conversion under paraffin isomerization conditions in the presence of a platinum reforming catalyst and then to conversion at conventional reforming conditions in the presence of a platinum reforming catalyst.

According to one concept of the present invention, the platinum reforming catalyst used for the paraffin isomerization can, and usually will, be a more active catalyst than the conventional platinum reforming catalyst. According to another concept of the invention, the platinum reforming catalyst is made more active by increasing the platinum content thereof to above that found in conventional platinum catalysts.

Another manner of increasing the activity of the catalyst is adding more fluorine thereto or by providing a more active silica-alumina base when one is employed. A combination of two or more of these means to increase catalyst activity can be used according to the invention. A greater amount of isopentane is produced by the process described in this embodiment than is normally produced at conventional reforming conditions. Also, it is possible to use rather low temperatures which, relatively speaking, are mild when compared with prior art operation.

In a second embodiment, the invention provides a process which comprises fractionating a debutanized, deisopentanized, deoiled natural gasoline into a normal pentane fraction and principally a C_6 and heavier fraction; isomerizing the normal pentane using a more active than normal reforming platinum-containing catalyst at a reaction temperature of approximately 700–800° F.; deisopentanizing the effluent; recycling the normal pentane to the isomerizer; reforming the C_6 and C_7 fraction under conventional platinum reforming conditions and combining the reformed fraction with the isopentane obtained from the isomerizer. The minimum platinum content of the catalyst will be about 0.6 percent. Preferably at least about 0.8 percent by weight of the catalyst will be platinum. The temperature with such a catalyst will not be in excess of about 800° F. when pentane or a pentane-containing stream is isomerized.

Another embodiment of this invention relates to a process which comprises fractionating a debutanized, deisopentanized, deoiled natural gasoline into a normal pentane-hexane fraction and principally a C_7 fraction, isomerizing the normal pentane-hexane fraction as described in the previous paragraph, for normal pentane alone, and reforming the C_7 fraction by conventional means. The reformed gasoline can be blended with the isopentane thus produced.

Thus, it will be seen that one of the features of the present invention involves separating out isopentane or a fraction containing the same before the remainder of the gasoline or fraction thereof is subjected to further conversion or reforming.

The hydrocarbon stocks that will be converted in accordance with my process comprise hydrocarbon fractions containing naphthenes and paraffins. This preferred class includes straight-run gasolines, natural gasolines, and the like. The gasoline may be full boiling range gasoline having an initial boiling point of from about 50° to about 100° F., and an end boiling point within the range of from about 325° to about 425° F., or it may be a selected fraction thereof. The preferred fraction of natural gaso-

line is one containing principally normal pentane, and hexane and heptane fractions.

The use of a more active catalyst in the first step of the process permits the use of lower temperatures. The formation of isopentane by the isomerization of normal pentane is thermodynamically favored by the use of the lower temperatures. Therefore, the invention, which provides for lower temperatures in the first step, with removal of isopentane following said step, results in increased isopentane which, when blended together with the remainder of the gasoline, when it has been reformed, will increase the quality of the final product. The removal of isopentane intermediate the steps of the process is an important feature of the present invention. This isopentane is not desirably passed into the reforming of the said remainder of gasoline.

Any conventional platinum or palladium reforming catalyst can be used in the first reactor. Such a catalyst can also contain a halogen such as chlorine or fluorine and can be prepared by combining a halogen with, say, alumina, in, say, a proportion of about 0.1 percent to about 8 percent by weight of said alumina, on a dry basis, commingling a platinum-containing solution with the halogen-containing alumina and calcining. A preferred catalyst for use in isomerization step of the invention will contain more than about 0.6 weight percent of platinum, but usually are not more than about 1.5 weight percent; from about 0.4 to 2 weight percent fluorine and the remainder of the catalyst will be said more active base. This base usually is a synthetically produced hydrocarbon cracking catalyst or a component thereof.

The preparation of the base or cracking catalyst or component can be variously accomplished. Such preparations are described in the prior art. The cracking component may comprise any suitable cracking catalyst, natural or synthetic, and includes various aluminum silicates which can be acid-treated or synthetically produced cracking catalysts such as silica-alumina, silica-alumina-zirconia, silica-zirconia, and combinations of silica with magnesia, alumina, thoria, boria, etc. The specific steps of preparation may include separate sequential or co-precipitation operations which are also described in the art. One such operation is accomplished by commingling an acid such as hydrochloric acid with commercial water glass to precipitate silica, washing with acidulated water to remove sodium and commingling with, say, aluminum sulfate following which ammonium hydroxide is added and the mass thus obtained dried and thermally decomposed to obtain the desired oxide or oxides. As noted, other methods can be employed to prepare the cracking component which ordinarily is calcined at a temperature within the range of from about 500 to 1400° F. before the platinum or palladium is admixed therewith.

In the second step, or steps in which the gasoline, from which a substantial proportion of isopentane has been removed, is reformed, the catalyst can be a conventional reforming catalyst, as already described, or as available in the art. A catalyst for reforming the gasoline or fraction from which the isopentane has been removed, according to this invention, will be one which contains from about 0.01 to about 1 weight percent platinum and from about 0.1 to about 8 percent fluorine or chlorine upon an active silica-alumina base or a cracking catalyst component. However, here, as before noted, the active base or the cracking component of the catalyst can be either a naturally occurring or synthetically produced material. Thus, naturally occurring cracking catalysts include various silicates such as aluminum silicates, which may have been acid treated to increase their activity. Also, the cracking component can be a silica-alumina, silica-alumina-zirconia, a silica-zirconia, silica-magnesia, silica-magnesia-alumina, silica-alumina-thoria, alumina-boria, etc., which have been synthetically produced by known methods. Such methods include successive impregnation, coprecipitation, trituration, etc.

In the lieu of platinum in the catalyst, palladium can be employed. Also, mixtures of platinum and palladium can be employed. Ordinarily, the cracking component is dried at a temperature of from about 350 to about 500° F., and is then calcined at a temperature of from about 500 to about 1400° F., before admixing or otherwise adding the platinum thereto. One method of adding the platinum or palladium to the cracking component is to add it to the dry cracking component in the presence of ammonium hydroxide, say, by commingling chloroplatinic acid with ammonium hydroxide to form a mixture of pH within the range of from about 5 to about 10 and then commingling this mixture with the preformed particles of the cracking component or base. Other methods of forming the catalyst, as described in the art, can be employed.

The reforming reactions of the invention are generally endothermic; therefore, the reaction streams passing between the reaction zones are reheated to a desired temperature.

The operating conditions in the first reactor, as noted, are maintained favorable for paraffin isomerization with little naphthene dehydrogenation. The conditions in the isomerization step of the process usually will be: a temperature from about 700° to about 800° F., a pressure of from about 100 to about 750 p.s.i.g., a liquid hourly space velocity of from about 0.2 to about 20, and a hydrogen to hydrocarbon ratio of from about 0.2 to 5 to 10 or more mols of hydrogen per mol of hydrocarbon. Conditions outside the ranges here given are within the scope of the invention to the extent that they function in a combination of steps here claimed to provide the beneficial results here set forth.

Reforming operations in the second and third reactor ordinarily will be conducted at temperatures of from about 800° to about 1000° F., preferably 850°–975° F., pressures within the range of from about 100 to about 1000 p.s.i.g., preferably about 200–700, with a liquid hourly space velocity of from about 0.2 to about 20. The amount of hydrogen charged along with the hydrocarbons usually will be from about 0.5 to about 15 mols per mol of hydrocarbon and preferably 6 to about 10 mols hydrogen per mol of hydrocarbon.

According to the invention, the isomerization is operated at a lower temperature (700–800° F.) than the reforming (800–1000° F.) and, as noted, a more active catalyst is used for isomerization than the conventional reforming catalyst. This use of a more active platinum reforming catalyst in the isomerization step permits an increase in the isomerization of the normal pentane obtained and permits the use of lower temperatures.

In Figure 1 of the drawings there is shown diagrammatically an embodiment of the invention in which in the first step only one reactor is employed and in which the second step or stage is conducted in two reactors in series arrangement. A fractionator is shown for the intermediate removal of the isopentane, according to the invention. In Figure 2, a normal pentane-containing stream and a hexane- and heptane-containing stream, which can be obtained by fractionating a single feed to the unit according to the invention, are, respectively, isomerized and reformed, the products of the two steps being then blended together.

Referring now to Figure 1 of the drawing, a natural gasoline which has been debutanized, deisopentanized and deoiled is passed through a heater (not shown) wherein it is raised to a temperature of about 750° F. Hydrogen is mixed with the heated gasoline in the approximate mol ratio of 1:1 and the mixture is passed through lines 11 and 12 into the isomerization reactor 13 which contains the catalyst which has approximately the following composition by weight: 0.7 platinum, 0.8 fluorine and the remainder consisting essentially of the silica-alumina base, as described, for isomerization. This catalyst, as noted, can be a conventional platinum re-

forming catalyst or, as preferred, according to the invention, is a more active platinum reforming catalyst, also as previously described. The gasoline along with hydrogen is passed through the reactor **13**. In the example here illustrated, the catalyst is deposited as a fixed bed in reactor **13**. It is to be understood that any other suitable manner of intimately contacting the reactants with the catalyst can be employed. The pressure in reactor **13** is about 300 p.s.i.g. and liquid hourly space velocity is about 0.3. The effluent from reactor **13** is passed through line **14** to hydrogen separator **15** wherein ordinarily all the hydrogen is removed through line **16** and recycled to reactor **13**. The balance of the effluent is passed through line **17** to a fractionator **18**, wherein the effluent is deisopentanized. The isopentane is removed through line **19** for outside use such as blending with a reformed gasoline, in this instance the reformed gasoline of the embodiment, in a blending vessel not shown. The bottoms from fractionator **18** is removed through line **20** and the temperature raised to about 850° F. in a heater (not shown) and passed together with hydrogen from line **21** to reactor **22**. The reformed gasoline from reactor **22** is passed through line **23**, heated, and into reactor **24**. The reforming catalyst deposited in reactor **22** and **24** has the following composition: 0.41 weight percent platinum, 0.24 weight percent fluorine, 0.23 weight percent chlorine, about 0.10 weight percent silica, and the balance alumina. In the case here illustrated, the catalyst is deposited as a fixed bed in reactors **22** and **24** but it is understood that any other suitable manner of intimately contacting the reactants with the catalyst may be used. A pressure of about 280 p.s.i.g. and a liquid hourly space velocity of about 0.3 are employed in reactors **22** and **24**. The amount of hydrogen charged along with the hydrocarbons is maintained in the range of 6 to about 10 mols hydrogen per mol of hydrocarbon, though in some instances, this ratio can vary in the range of from 0.5 to about 15.

The distribution of hydrogen to reactors **13**, **22**, and **24** is controlled to maintain the desired hydrogen concentration in each of these reactors. Preferably a greater hydrogen concentration is maintained in reactors **22** and **24** than in reactor **13**. When the supply of hydrogen in the process is not sufficient, additional hydrogen is introduced from an extraneous source through line **25**. When the amount of hydrogen produced in the process is in excess of that desired, the excess hydrogen is removed from the process by way of line **25**.

Ordinarily little or no hydrogen will be made in reactor **13** and for this reason, all of the hydrogen from separator **15** will be recycled through line **16**. Since, ordinarily, the hydrogen from reactors **22** and **24** will be sufficient to supply the hydrogen for reactor **13**, the make-up hydrogen for reactor **13**, when supplied through line **25**, can come from the separation of hydrogen from the reformate, now mentioned.

The reformate is removed from reactor **24** through line **26** for subsequent separation and recovery (not shown). Usually this separation will include stabilization of the gasoline to produce a final gasoline of desired vapor pressure.

When isopentane is to be blended with the reformate, it can be introduced into admixture therewith by way of line **27** to the extent or in proportion, as desired.

By operating according to the process of the present invention, that is, by first isomerizing followed by reforming, with intermediate removal of isopentane, as described herein, a greater amount of isopentane is produced than by conventional reforming.

A debutanized deoiled natural gasoline is fractionated into a C_5 and a C_6–C_7 fraction. The C_5 fraction is isomerized over a more active than usual platinum catalyst as described herein, and the C_5 reformate thus obtained is fractionated into iso and normal pentane. The isopentane is blended with a C_6–C_7 reformate obtained from said C_6–C_7 fraction over a conventional platinum-reforming catalyst.

The following data show the gain obtained upon increasing the platinum content of the catalyst from 0.4 to 0.8 weight percent platinum.

A conventional catalyst of the platinum-reforming type contains about 0.4 to about 0.6 weight percent platinum.

Platinum, wt. percent	0.4	0.8
Pressure, p.s.i.g.	150	150
Temperature, ° F.	820	820
LHSV	3	3
H_2/HC, mol	3	3
n-C_5 conversion, wt. percent	51	54
Selectivity, wt. percent	88	90
Yield of i-C_5, wt. percent	45	49

From the foregoing data, it will be noted that the conversion of normal pentane, the selectivity and the yield of isopentane obtained with the catalyst containing 0.8 weight percent platinum are considerably and importantly higher than those obtained with the catalyst containing 0.4 weight percent platinum.

The foregoing data illustrate the importance of increasing the platinum content in the catalyst in the first step.

The following illustrates the results which can be obtained according to the second step of the combination of steps of the invention.

A sample of deoiled, debutanized natural gasoline, see Table I, column 3, was fractionated to remove isopentane, and the normal pentane and heavier material were reformed at normal reforming conditions as in the embodiment just described. The C_5+ liquid volume percent yield from the reforming operation was 93.6 and the octane ratings of the natural gasoline, reformer feed, and C_5+ reformate were:

	Research+3 TEL	Research Clear
Natural Gasoline	90.0	72.7
Feed, Deisopentanized Natural Gasoline	84.0	65.1
C_5+ Product (93.6 vol. percent yield)	92.6	78.6

Blending the isopentane from the fractionation back with the C_5+ product gave a 95.4 overall liquid volume percent yield of product having a Research +3 TEL rating of 96 (calculated). Data for this work are in Tables I and II hereinafter.

TABLE I

Deisopentanization of natural gasoline

Fraction	Isopentane	Normal Pentane and Heavier	Natural
LV Percent of Natural Gasoline	27.8	72.2	100.0
Composition, wt. percent:			
Butane	7.8	0.0	----------
Isopentane	87.0	2.1	----------
Normal Pentane	5.2	36.4	----------
C_6+	0.0	61.5	----------
Total	100.0	100.0	----------
API Gravity (60° F.)	96.4	78.3	82.8
RVP	22.20	9.50	12.95
ASTM Distillation:			
IBP	79	108	95
5%	79	119	103
10	79	123	106
20	79	125	109
30	80	129	112
40	81	133	116
50	82	139	122
60	83	146	130
70	84	155	139
80	85	169	155
90	87	186	181
95	87	200	199
EP	137	246	254
Recovered, percent	96.2	98.2	98.0
Residue, percent	----------	0.4	0.4
Loss, percent	3.8	1.4	1.6
Octane Rating:			
Research+3 ml. TEL	104.0	84.0	90.0
Research, Clear	92.1	65.1	72.7

TABLE II

Reforming of deisopentanized natural gasoline

Process conditions:	
Temp., ° F.:	
Average	877
Preheat	888
Bottom of bed	887
Liquid sp. vel., vol./cat. vol./hr.	3.1
Hydrogen/naphtha, mol ratio	6.5
Pressure, p.s.i.g.	500
Product yields, wt. percent of feed:	
H_2	0.1
CH_4	0.5
C_2's	0.5
C_3's	1.8
C_4's	3.0
iC_5	20.6
nC_5	21.8
C_6+	51.7
Total	100.0
C_5+ Product:	
Yield, LV percent	93.6
API gravity (60° F.)	77.4
RVP	10.75
ASTM distillation—	
IBP	101
5%	114
10	116
20	120
30	124
40	128
50	134
60	140
70	151
80	164
90	185
95	206
EP	266
Recovered percent	97.7
Residue percent	0.5
Loss percent	1.8
Octane rating—	
Research +3 ml. TEL	92.6
Research, clear	78.6

It will be apparent to one reading this disclosure that the catalysts employed in the several steps of the process can be various and different and, therefore, in respect of the combination of steps claimed, it is not limited to any particular catalyst except as in the claims. However, the now preferred catalysts have been described and to this extent, their combination with the remainder of the steps is a part of the claimed invention.

Although the preferred catalyst for the first step of the invention will usually contain more than about 0.6 weight percent of platinum, it is possible, in a broader view of the operation to employ in said step a catalyst containing from about as low as 0.01 percent platinum to about 1 percent platinum by weight of the final catalyst as used.

Referring to Figure 2 of the drawing, a heated mixture of hydrogen and normal pentane is passed through line **30** into the isomerization reactor **31**. Reactor **31** contains a catalyst comprising about 0.6 weight percent platinum and 0.6 weight percent fluorine on alumina. The operating conditions are a total pressure of 500 p.s.i.g., a liquid hourly space velocity of 4 and a temperature of 700–800° F.

The effluent from reactor **31** is withdrawn through line **32** to a hydrogen separation zone **33**. Hydrogen is removed through line **34** and recycled to reactor **31**. The balance of the effluent is removed through line **35** to fractionator **36** wherein isopentane is removed overhead through lines **37** and **38** to be blended with normal pentane and the C_7 and C_6 reformate. Normal pentane is removed from the fractionator **36** through lines **39** and **30** back to the isomerization reactor **31** or part of the normal pentane may be removed if desired through lines **39**, **40** and **38** to be blended with isopentane and the C_6 and C_7 reformate. A heater (not shown) is required to heat the recycle normal pentane to the reactor **31**.

The C_6 and C_7 fraction is passed through line **41** and is joined by a stream of recycle hydrogen flowing through line **42**. The commingled streams are passed through a heater (not shown) wherein they are heated to the desired temperature and through line **43** into reactor **44**.

Reactors **44** and **45** each contain a bed of platinum reforming catalyst comprising about 0.3 percent platinum and 0.1 percent fluorine on alumina and the conditions therein are a pressure usually in the range 300–700 p.s.i.g., a hydrogen/hydrocarbon ratio of 5:1, a temperature in the range from about 850 to about 975° F., and a liquid hourly space velocity of about 4.

The effluent from reactor **44** is withdrawn through line **46** through a heater (not shown) into reactor **45**. The operating conditions in reactors **44** and **45** are approximately the same. The effluent from reactor **45** is withdrawn through line **47** to a hydrogen separation zone **48**, wherein hydrogen is removed through line **49** and recycled to reactor **44** or a portion transferred through lines **49**, **34** and **30**, to reactor **31**. When the supply of hydrogen in the process is not sufficient, additional hydrogen may be introduced from an extraneous source through line **50**. On the other hand, when the amount of hydrogen produced in the process is in excess of that desired, the excess hydrogen may be removed from the process by way of line **50**.

The C_6 and C_7 reformate is withdrawn from zone **48** through line **51** for subsequent separation and recovery (not shown). Usually this separation will include stabilization of the gasoline to produce a final gasoline of desired vapor pressure.

As noted earlier herein, the respective feeds to reactors **31** and reactor **44** can be a pentane-containing stream and a hexane- and heptane-containing stream obtained by way of a fractionation of a single feed to the unit. Such a fractionation is not shown in the drawing for sake of simplicity. Clearly, it is the essence of the invention to treat separate streams, as described, derived from a natural gasoline in a manner as described herein and as set forth in the drawings.

An embodiment of this invention is, as noted, a process which comprises fractionating a debutanized, deisopentanized, deoiled natural gasoline into a normal pentane-hexane fraction overhead and principally a heptane bottom fraction, isomerizing the normal pentane-hexane portion and reforming the heptane fraction by conventional means.

In the reforming of natural gasoline one of the principal desirable reactions is isomerization of the normal pentane and normal hexane. When platinum-containing catalysts are used, increased isomerization of the normal pentane and normal hexane can be obtained by segregating a normal pentane-hexane fraction and a heavier fraction, contacting the normal pentane-hexane fraction with a higher acidity platinum catalyst and the heavier fraction with a lower acidity catalyst. The use of a higher acidity catalyst gives isomerization of the normal pentane-hexane because the catalyst is more active and tends to give more isomerization at any temperature and also because the more active catalyst permits the use of lower temperatures at which the formation of branched pentane and hexane hydrocarbons is thermodynamically favored. The lower acidity catalyst is desirable with the heavier fraction because it gives more efficient conversion of naphthenic hydrocarbons to aromatics. When platinum-fluorine-alumina catalysts are used, it is prefer-

able to have about 0.4 to 1.0 percent fluorine in the high acidity catalyst and 0.1 to 0.3 percent fluorine in the lower acidity catalyst.

A 150–270° F. naphtha was contacted with two platinum-halogen-alumina catalysts having the following compositions:

Catalyst	1	2
Composition, wt. percent:		
Platinum	0.4	0.4
Fluorine	0.5	0.2
Chlorine	0.0	0.2
Alumina	99.1	99.2
Total	100.0	100.0

The compositions of the xylene-ethylbenzene fractions of the products are an index of the isomerization activity of the catalysts. Catalyst 1 (higher fluorine) gave a larger amount of isomerization, even at lower temperature, as is shown by the following data.

Catalyst	1	2	2
Run No	A	B	C
Temp., °F	876	876	888
Pressure, p.s.i.g	415	415	415
LHSV	3.6	3.7	3.6
H_2/HC	7.5	7.5	6.7
Xylene-ethylbenzene fraction, wt. percent:			
p-xylene	19.2	17.3	17.8
m-xylene	42.7	37.3	36.7
o-xylene	18.7	21.1	19.7
Ethylbenzene	19.4	24.3	25.8
	100.0	100.0	100.0

The data show that catalyst 1 gave higher isomerization of ethylbenzene to xylenes.

Reasonable variation and modification are possible within the scope of the foregoing disclosure, drawings and the appended claims to the invention, the essence of which is that a natural or straight-run gasoline or a component thereof, specifically a pentane-containing stream, is subjected to conditions favoring isomerization of paraffin hydrocarbon therein; in one form of the invention, the reforming of pentane in a stream containing it being accomplished employing a more active platinum reforming catalyst, as described, at a temperature not in excess of about 800° F.; preferably after debutanization, deisopentanization and deoiling; the isomerized gasoline or component thereof constituting said stream is fractionated to remove isopentane therefrom and the remainder of the gasoline or component thereof is reformed in at least one embodiment of the invention, the isopentane and reformed remainder are blended together in a proportion, as desired, to obtain, from the process, improved yields of isopentane from at least one of the isomerization and the reforming steps and an improved product, as described. Herein and in the claims, platinum and palladium are considered to be functionally interchangeable.

I claim:

1. A process for up-grading a natural gasoline containing pentane in which process it is desired to obtain high octane value reformed gasoline product formed in a reforming zone in the absence of substantial amounts of normal pentane contained in said gasoline which comprises in a first step subjecting the gasoline to conditions favoring paraffin isomerization reactions thus providing for the formation therein of improved yield of isopentane from normal pentane contained therein thus substantially reducing the normal pentane content of said natural gasoline, removing a substantial portion of isopentane from the thus treated gasoline thus obtaining a remaining gasoline substantially freed from normal pentane and isopentane and then subjecting the remaining gasoline to reforming conditions to reform the same.

2. A process according to claim 1 wherein at least a portion of the removed isopentane and at least a portion of the said remaining gasoline which has been reformed are blended to produce a gasoline product.

3. A process for up-grading a gasoline selected from the group consisting of natural and straight-run gasolines in which process it is desired to obtain high octane value reformed gasoline product formed in a reforming zone in the absence of substantial amounts of normal pentane contained in said gasoline which comprises debutanizing, deisopentanizing and deoiling said gasoline, then subjecting said gasoline to conditions favoring isomerization of normal pentane therein so as to isomerize a substantial portion of said pentane to isopentane thus substantially reducing the normal pentane content of said natural gasoline, separating a substantial quantity of said isopentane from said gasoline thus obtaining a remaining gasoline substantially freed from normal pentane and isopentane, subjecting the remainder of the gasoline to reforming conditions so as to reform the same thus obtaining as products of the process isopentane and a reformed gasoline which can be blended together to give an improved gasoline product.

4. A process according to claim 3 wherein in the first treating step a temperature in the approximate range 750 to 800° F., a pressure in the approximate range of 250 to 750 p.s.i.g. and a liquid hourly space velocity of 0.2 to about 5 are employed in the presence of a catalyst which will favor isomerization of pentane to isopentane under the said conditions.

5. A process according to claim 4 wherein hydrogen is employed in a molar ratio of hydrogen to hydrocarbon of from about 0.2 to about 5 mols of hydrogen per mol of hydrocarbon.

6. A process according to claim 5 wherein the catalyst in said step wherein pentane is isomerized to isopentane contains from 0.6 to about 1 weight percent platinum, and from about 0.4 to about 2 weight percent fluorine upon an active silica-alumina base.

7. A process according to claim 3 wherein in said reforming step a temperature in the range of from about 800 to about 1000° F., a pressure within the approximate range of 250 to 1000 p.s.i.g., a liquid hourly space velocity of 0.2 to about 20 and a mole ratio of hydrogen to hydrocarbon of from about 0.5 to about 15 are employed.

8. A process according to claim 7 wherein in said reforming step a catalyst containing from about 0.01 to about 1 weight percent platinum and from about 0.1 to about 8% fluorine upon an active silica-alumina base is employed.

9. A process for upgrading a natural gasoline in which process it is desired to obtain high octane value reformed gasoline product formed in a reforming zone in the absence of substantial amounts of normal pentane contained in said gasoline which comprises subjecting said gasoline to isomerization conditions thus isomerizing its pentane content therein to isopentane thus substantially reducing the normal pentane content of said natural gasoline, reforming a fraction of said gasoline which contains hydrocarbon higher boiling than pentane and from which substantially all pentane has been removed and blending together the isopentane and reformed product thus obtained.

10. A process for upgrading the gasoline selected from the group consisting of a natural gasoline and a component thereof which comprises in a first step subjecting the same to conditions favoring paraffin isomerization reactions thus providing for the formation of improved yield of isopentane from normal pentane therein contained, removing the isopentane from the thus obtained product and then subjecting the remainder of the product to reforming conditions to reform the same.

11. A process according to claim 10 wherein at least a portion of the removed isopentane and at least a portion of the remaining product are blended to produce a final product.

12. In a hydrocarbon conversion operation in which a fraction containing normal pentane is first isomerized

and the fraction then reformed, the improvement which comprises substantially removing isopentane produced in said isomerization before conducting the reforming and then conducting the said reforming upon the remainder of said isomerized fraction.

13. A process for the improvement of a gasoline selected from the group consisting of a debutanized natural gasoline and a straight run gasoline which contain normal pentane comprising contacting said gasoline at a temperature in the range of 700° F. to 800° F. with a supported platinum isomerization catalyst containing at least about 0.6 percent platinum by weight of the catalyst and a halogen selected from the group consisting of chlorine and fluorine in the range of 0.1 to 8 percent by weight of the support, separating the isopentane from the effluent, contacting any unconverted normal pentane and higher boiling gasoline components remaining after the separation of isopentane with a platinum-containing reforming catalyst under reforming conditions including a higher temperature in the range of 800° to 1,000° F. whereby additional isopentane is produced and the octane number of the higher boiling fraction is increased.

14. A process according to claim 1 wherein in the first step the catalyst is a platinum catalyst containing at least about 0.7 percent by weight platinum, about 0.8 percent by weight fluorine, the remainder consisting essentially of a hydrocarbon cracking catalyst base.

15. A process according to claim 14 wherein the platinum-containing catalyst in the reforming step contains 0.01–1 percent by weight of the catalyst of platinum and 0.1–8 percent by weight of said halogen upon an active cracking catalyst component.

16. A process according to claim 1 wherein the isomerization conditions include a temperature in the range 700° F.–800° F. and the reforming step is conducted at a temperature in the range 850° F.–975° F. at a pressure in the range 100–1,000 p.s.i.g., a liquid hourly space velocity of 0.2–20 and 0.5–15 mols hydrogen per mol of hydrocarbon is present.

References Cited in the file of this patent

UNITED STATES PATENTS

2,276,171	Ewell	Mar. 10, 1942
2,443,607	Evering	June 22, 1948
2,479,110	Haensel	Aug. 16, 1949
2,626,893	Morrow	Jan. 27, 1953
2,651,597	Corner et al.	Sept. 8, 1953
2,664,386	Haensel	Dec. 29, 1953
2,740,751	Haensel et al.	Apr. 3, 1956
2,798,105	Heineman et al.	July 2, 1957
2,818,449	Christensen	Dec. 31, 1957
2,900,323	Patton et al.	Aug. 18, 1959