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3,136,825

PROCESS FOR DISPROPORTIONATION OF ISOPARAFFINIC HYDROCARBONS

Patrick W. Ryan, Chicago Heights, Ill., Ronald S. Bartlett, Lafayette, Ind., and Robert A. Sanford, Homewood, Ill., assignors, by mesne assignments, to Sinclair Research, Inc., New York, N.Y., a corporation of Delaware

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The present invention relates to a process for the conversion of low octane number paraffin feedstocks into higher octane rating motor fuel components. More particularly, the present invention relates to a process of paraffin disproportionation whereby higher molecular weight paraffins react with lower molecular weight paraffins to produce intermediate molecular weight paraffins boiling in the gasoline range.

In recent years the automobile manufacturers have steadily increased the compression ratios of their spark ignition engines as a means of obtaining more power and greater efficiency. As the compression ratios of the engines increase, the hydrocarbon fuel employed must be of higher octane value to provide efficient knock-free operation notwithstanding that fuel octane can be increased through the addition of tetraethyl lead; and other undesirable aspects of engine operation, for instance pre-ignition, can be overcome by the use of other additive components. Thus the problem remains for petroleum refiners to produce higher octane base hydrocarbon fuels under economically feasible conditions.

These refiners now have installed a substantial number of units for reforming straight run petroleum fractions in the presence of free hydrogen and over a platinum metal-alumina catalyst to obtain relatively high octane products. Primarily these products, frequently called reformates, are blended with other gasoline components such as thermal and catalytically cracked gasolines, alkylate, etc., and additives such as tetraethyl lead in obtaining present-day motor fuels. The reforming operation has a number of disadvantages. First, as the octane requirements of the blended engine fuels rise, the octane quality of the reformate must also increase if the blends be otherwise unaltered. This increase results in a substantial reduction in yield particularly when obtaining reformates having octanes (RON neat) of the order of 90 to 95 or above. As the severity of the operation is increased, the platinum metal-containing catalyst becomes fouled more often with carbonaceous deposits which requires more frequent regenerations and/or replacements. As the platinum metal-alumina catalysts are relatively expensive, either replacement or withdrawal from use during regeneration materially increases the cost of providing a given volume of reformate. These and other factors affecting the yield-octane number-cost relationship make it desirable for the refiner to consider various ways in which high octane hydrocarbon fuel components can be obtained by employing processing methods other than platinum metal-alumina catalyst reforming operations.

A source of further octane enhancement lies in upgrading relatively low octane paraffins as, for instance, by paraffin disproportionation. A number of catalyst systems are known as being useful in this type of operation and such catalyst systems include, for example AlCl_3/HCl , HF/BF_3 and HF . These catalysts have not proven entirely satisfactory, however, in that they age rapidly and form large amounts of catalyst oil. The HF catalyst systems have the additional disadvantages in that HF is highly corrosive and difficult to handle.

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The present invention relates to a process for upgrading low octane, normally liquid isoparaaffinic feedstocks, for instance, having a neat octane rating (RON), up to about 75, preferably up to about 60, by way of disproportionation in a boron trifluoride-phosphoric acid catalyst system. Generally, a gain in octane number of about 10 or greater is obtained. The present process has particular advantage in that it can be utilized in conjunction with reforming systems employing gasoline feedstocks and platinum-alumina catalysts to upgrade the isoparaaffinic feeds commonly obtained from reformates, as, for example, by the Udex or other solvent extraction or separation processes. Moreover, since our process is selective in converting isoparaaffins, any unreacted normal paraffins in the feedstock can be used as turbine engine fuels or recycled to reforming or isomerization systems for conversion into higher octane rating components.

In accordance with the present invention an isoparaaffinic feedstock of about 6 to 12 carbon atoms and isobutane are contacted with a boron trifluoride-phosphoric acid catalyst in a disproportionation zone and a product boiling in the gasoline range having an increased octane rating is obtained. The disproportionation is at a temperature of about 30°F . to 350°F ., preferably about 200 to 275°F .; and a BF_3 partial pressure sufficient to maintain the hydrocarbon mixture at least partially in a liquid state, for instance, about 100 to 5000 p.s.i.g., preferably about 600 to 1200 p.s.i.g. The hydrocarbons are contacted with the catalyst for a time sufficient to substantially increase the octane rating of the resulting product boiling in the gasoline range. Normally, this period will be dependent on the stirring efficiency, temperature and BF_3 partial pressure but will generally fall within the range of about 15 minutes to 5 or more hours, preferably about 1 to 2 hours. The ratio of the heavier isoparaaffin to isobutane is generally about 0.1:1 to 10:1, preferably about 0.7:1 to 2:1. Advantageously, these reaction conditions are selected to provide conversion of at least about 60%, preferably at least about 90 or 95%, of the heavier isoparaaffinic feed to lower boiling hydrocarbons.

The phosphoric acid catalyst of the present invention is employed in effective catalytic amounts and will usually be present in the disproportionation zone in a weight ratio of about 0.1:1 to 10:1 of total hydrocarbon to catalyst, preferably in a weight ratio of about 0.3:1 to 2:1. The process may be carried out in a batch operation or in a continuous operation which provides for recycle of the catalyst and isobutane. In conducting the reaction, an overall isobutane consumption is preferred, for example, about 1 to 25%, preferably about 5 to 10% based on the isobutane charged.

The hydrocarbon product and the phosphoric acid-boron trifluoride catalyst layers resulting on completion of the reaction can be separated by any manner desired. When agitation of the reaction mixture is stopped, it will separate into two phases in the reactor or in any other vessel into which it is transferred as in a continuous or batch operation. These phases can be separated by simple decantation.

The reaction mixture can be allowed to separate into a lower layer of catalyst containing unsaturated oil including aromatics. The upper hydrocarbon layer formed can be freed from the catalysts by distillation and/or washing with water or passed through a column of basic ion exchange resin or other solid absorbent such as charcoal, potassium sulfate, sodium sulfate, etc. The unsaturated oil (catalyst oil) appearing in the catalyst layer can be separated through discharge into water followed by extraction with a solvent, e.g. ether or pentane. Small

traces of fluoride remaining in the hydrocarbon material can be removed as by contact with alumina at about 200° to 500° F. Various drying procedures can be employed to separate the water from the hydrocarbon materials. Preferably the reaction product is characterized, aside from the C₄'s, by predominantly a C₅ to C₇ fraction with C₅ being a major component.

As aforementioned, the disproportionation reaction of the present invention is conducted under a BF₃ partial pressure of about 100 to 5000 p.s.i.g. In operation, therefore, phosphoric acid is saturated with BF₃ and the reaction medium provided with excess BF₃ to give the required partial pressure. It is preferred that the phosphoric acid saturated with BF₃ be about 40 or 50% to 100% concentration in water. The more concentrated phosphoric acid is preferred, e.g. at least about 80% since with increasing concentration there is less consumption of boron trifluoride. With 100% phosphoric acid, for instance, one mole of boron trifluoride is absorbed per mole of acid while in the case of aqueous solutions both the phosphoric acid and water absorb boron trifluoride approximately mole for mole. The phosphoric acid-boron trifluoride catalyst system may be preformed, that is, formed prior to addition of the hydrocarbon reactants or formed in situ, that is, after addition of the hydrocarbon reactants and phosphoric acid to the reaction zone.

The hydrocarbon feed of the present invention contains an isoparaffin feed of about 6 to 12 carbon atoms. Although pure isoparaffins either alone or mixed with each other can be used, advantageously, petroleum fractions in the C₆ to C₁₂ boiling range having at least about 50% by weight isoparaffins, preferably at least about 65% by weight in admixture with normal paraffins, and perhaps other hydrocarbons, of similar boiling range can be employed. Such materials are found in various petroleum refinery streams and can be separated in more or less pure form. If desired, large amounts of olefins may be excluded from our reaction system and we prefer an essentially olefin-free feedstock, for instance, having not more than about 5% olefins.

A particularly suitable feedstock is a paraffinic concentrate derived from the C₇+ liquid product contained in the effluent of reforming systems employing petroleum gasoline feedstocks and platinum-alumina catalysts. As an example, most if not all of the aromatics of the reformat can be separated as by adsorption, extractive distillation, or any other procedure desired. The paraffinic materials resulting are predominantly isoparaffinic containing in admixture about 15 to 35 weight percent normal paraffins with minor amounts of olefins, aromatics and naphthenes. To obtain this feedstock from the reformat, the aromatics can be adsorbed on silica gel; or separated by solvent extraction through the use of a solvent selective for aromatics, e.g. phenol, or by any other desirable procedure.

A particularly useful method for accomplishing this separation employs a glycol-water extraction medium. As commercially licensed, one such system is known as Udexing. By regulation of conditions such as a glycol to water ratio, the extraction and solvent stripping temperature, and the character of the glycol, a Udex raffinate varying in paraffinicity is obtained. The manner of controlling these factors is known in the art and it is sufficient to say that the preferred glycol materials are the glycols such as diethylene and dipropylene glycols and their mixtures.

In a preferred embodiment this invention provides a method of obtaining higher octane fuels for spark ignition engines involving the use of separate reaction zones in which are employed catalysts of different properties. In this method a gasoline, including naphtha, is contacted with a platinum metal alumina catalyst in the presence of free hydrogen under conditions which provide a substantial increase in the octane number of the petroleum hydrocarbon material. A low octane isoparaffin fraction,

for instance, boiling predominantly in the C₈-C₉ range, of the resulting reformat is separated and then contacted with isobutane and with the boron trifluoride-phosphoric acid catalyst in a disproportionation zone to give a product boiling in the motor fuel which is of substantial octane rating.

The hydrocarbon feedstocks charged to the reaction zone containing the platinum-metal-alumina catalyst are petroleum fractions boiling primarily in the gasoline range, for instance in the range from about 175 to 450° F., but somewhat higher or lower boiling constituents can be included if desired. Preferably, the feedstock boils primarily in the range of about 200 to 400° F. Although the hydrocarbons passing to the platinum metal-alumina catalyst reaction system may be composed of predominantly saturated or straight run naphtha material, additional components can be used by themselves or in admixture. Such components include thermal and catalytically cracked stocks, particularly when hydrogenated, recycled reformat fractions of these cracked and reformed materials, etc. The reaction conditions observed or maintained in the platinum metal-alumina catalyst system include those suggested for present commercial reforming operations such as temperatures from about 750 to 1000° F., preferably about 825 to 975° F., and pressures from about 50 to 1000 p.s.i.g., preferably about 150 to 500 p.s.i.g. The free hydrogen supplied to this reaction system usually is in the form of hydrogen-rich recycle gases and generally provides about 2 to 20 moles of hydrogen per mole of hydrocarbon feed; preferably this ratio is about 4 to 10:1. The space velocity usually lies in the range of about 0.5 to 10 WHSV (weight of feed per weight of catalyst per hour) preferably about 2 to 5 WHSV.

The platinum metal-alumina catalysts employed in the method of this invention include a number of compositions. Generally, the platinum metal is a minor amount of the catalyst, e.g. about 0.1 to 1.5 weight percent of the final composition. Platinum is the most commonly employed metal present in these reforming catalysts although other useful platinum metals include rhodium, palladium, iridium which, along with platinum, are the face centered cubic crystallite types of the platinum family as distinct from the hexagonal types ruthenium and osmium which appear to be of lesser value.

A paraffin-rich fraction of the liquid reformat from the platinum metal catalyst operation is obtained as a Udex raffinate as noted above and contains predominantly isoparaffins together with about 15 to 35 weight percent of normal paraffin constituents with minor amounts of naphthenes, aromatics and olefins. The feedstock boils primarily in the motor fuel range, for instance, from C₇ up to about 425° F., although heavier constituents can be included.

This paraffin-rich feed obtained as a Udex raffinate is then contacted with the phosphoric acid-boron trifluoride catalyst system in the presence of isobutane as previously described. Normal paraffins may be present since they do not inhibit the reaction. In the system of the present invention primarily the isoparaffins of the feedstock react, with their being preferably little, if any, conversion of normal paraffins.

The disproportionate may be further processed in several ways. For instance, the disproportionate may be subjected to distillation to recover isobutane which could then be recycled. The C₅+ fraction which has a high octane number could be sent to the gasoline pool or could be passed over a 5 A. molecular sieve in order to obtain a high octane C₅-C₉ gasoline and recover the unreacted C₈ and C₉ normal components.

If desired the C₅+ disproportionate could be further processed as, for example, by subjecting it to further distillation to obtain a high octane C₅-C₇ cut which can be sent directly to the gasoline pool and a bottoms fraction which contains small amounts of isoparaffinic C₈'s and C₉'s and larger amounts of normal C₈ and C₉ paraffins.

The low octane bottoms fraction from this distillation is a poor recycle stock due to its high content of normal paraffins. However, it can be further processed by sending it as a feed to a catalytic reformer where the normal paraffins are converted to aromatic and isoparaffins. The resulting reformat could then be recycled and disproportionated, or first, dearomatized and the raffinate subjected to further disproportionation. Other processing alternatives obvious to those skilled in the art can be employed.

The following examples will serve to further illustrate the present invention and the improved results obtained thereby.

EXAMPLE I

A boron trifluoride saturated solution of 100% phosphoric acid was charged to a 1-gallon autoclave. The temperature was raised to approximately 252° F. and a mixture of isobutane and a C₆ to C₉ sulfuric acid-treated naphtha reformat cut was pressured into the reactor by means of a calibrated blowcase. The C₆ to C₉ reformat cut employed analyzed as follows:

Paraffins, vol. percent	82.9
Olefins, vol. percent	0.0
Naphthenes, vol. percent	14.6
Aromatics, vol. percent	2.5
Composition, vol. percent:	
C ₆	3.2
iC ₇	55.0
iC ₈	29.4
nC ₈	8.0
iC ₉	4.4
nC ₉	
Octane number (RON+3 cc. TEL added/gal.)	73.8

The reactor was then pressured up with BF₃ to approximately 985 p.s.i.g. and stirred for 2 hours after which stirring was stopped. The reactor was then cooled. The contents of the reactor were drained into a room temperature trap, which was in reality a separatory funnel. The room temperature trap was connected to a series of four cold traps where condensable gases were collected. After the catalyst was collected in the room temperature trap it was drained and stored in a tapered stoppered bottle. The hydrocarbon in the room temperature trap was collected and weighed. The hydrocarbon present in each of the four cold traps was also weighed. The total hydrocarbon weight (447 g.) showed a weight percent recovery of 90.2% (excluding catalyst oil).

The hydrocarbon products (excluding catalyst oil) were combined and analyzed. The results of the run are shown in Table I.

Table I

Run number	41.
Feedstock	Acid treated reformat.
iC ₄ /total H'C wt. ratio	0.471.
Catalyst	100% H ₃ PO ₄ /BF ₃ .
Catalyst gain, g.	165.
Catalyst/total H'C wt. ratio	1.
Temperature, ° F.	252.
Pressure	985.
Product g. (wt. percent)	447 (90.2).
Debutanized product analyses,	
ASTM distillation:	
IBP	94.
10	118.
50	183.
90	468.
EP	≈500.
Percent rec.	90.5.
Percent res.	
Percent loss	
Octane No. (RON +3 cc. TEL/gal.)	84.2.

ES 45a:

P	87.7.
O	0.0.
N	10.8.
A	1.5.

FIA

O	0.0.
A	0.8.

The data clearly shows that low octane number isoparaffinic feedstocks may be advantageously disproportionated in the presence of isobutane and a phosphoric acid-boron trifluoride catalyst system to yield a higher octane product.

EXAMPLE II

A straight-run naphtha is obtained by distillation from crude oil, and the naphtha typically has an ASTM distillation boiling range of about 209 to 381° F., a RON (neat) of about 47.2, and a gravity API at 60° F. of about 56.7. This naphtha is fed to a reforming unit containing three essentially adiabatic reactors each having a fixed bed of a platinum-alumina reforming catalyst. This system is equipped with means for heating the charge to each reactor and the heaters and reactors are arranged for serial flow. The catalyst employed is a platinum-alumina reforming catalyst containing about 0.6 weight percent platinum, and manufactured in accordance with U.S. Patent No. 2,838,444. The inlet temperature of the feed to each of the three catalyst beds is 940° F., while the pressure is about 500 p.s.i.g. Free hydrogen is supplied to the feed passing to the heater before the first reactor and the hydrogen is supplied to the feed passing to the heater before the first reactor and the hydrogen is obtained by recycle from the third reactor effluent stream. The molar ratio of hydrogen-rich recycle gas (72.7% H₂) to hydrocarbon feed is approximately 5.5 to 1, while the overall space velocity is about 2.34 WHSV. The effluent from the last reactor is conveyed to a flash drum operating at 500 p.s.i.g. and is then treated or depropanized to remove C₃ and lighter hydrocarbons by distillation.

6.71 parts by volume of the resulting reformat are passed at a temperature of 222° F. to a distillation column having a top temperature of 215° F. and a bottom temperature of 336° F. to remove light gasoline boiling in a range of about 118 to 216° F. as overhead. 3.17 parts by volume of the bottoms of this distillation column are charged at 316° F. to another distillation column having a top temperature of 279° F. and a bottom temperature of 348° F. to remove a heavier gasoline fraction and an overhead fraction having a boiling range of about 250 to 284° F. 1.622 parts by volume of the overhead from the latter distillation column is sent to an extractor having a tower top and bottom temperature of 280° F. into which is fed 8.16 parts by volume of an extractive medium containing about 17% by volume of dipropylene glycol, 75.5% by volume of diethylene glycol and 77.5% by volume of water. The raffinate obtained as overhead from the extractor analyzed as follows:

Paraffins, vol. percent	88.3
Olefins, vol. percent	3.0
Naphthenes, vol. percent	6.7
Aromatics, vol. percent	2.0
Composition, vol. percent:	
C ₆	
iC ₇	45.4
iC ₈	14.9
nC ₈	36.5
iC ₉	3.2
nC ₉	
Octane number (RON +3 cc. TEL added/gal.)	60.8

The raffinate feedstock was then disproportionated in the presence of isobutane and either 85% or 100% H₃PO₄/BF₃ according to the method of Example I under the conditions shown in Table II below. The results are also shown in Table II.

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Table II

Run number.....	32	36
Catalyst.....	85% H ₃ PO ₄ /BF ₃	100% H ₃ PO ₄ /BF ₃
iC ₄ extract feed wt. ratio.....	1	1
Catalyst total H'C wt. ratio.....	1	1
Temperature.....	245	229
Pressure.....	1,040	1,060
Wt. percent recovery.....	98.9	99.6
Wt. percent catalyst oil.....	4.7	7.0
Product distribution:		
C ₃	3.1	2.6
C ₄	47.3	48.8
C ₅	23.6	26.1
C ₆	10.5	9.0
C ₇	3.6	3.1
iC ₈	2.6	2.1
n-C ₈	7.3	5.8
iC ₉	1.4	1.1
n-C ₉	0.6	1.3
Wt. percent conversion.....	77.3	80.8
C ₅ , C ₆ , C ₇ yield.....	72.0	71.2
Octane No. RON + 3 cc.'s TEL/gal.....	87.7	87.5
Vol. percent yield.....	107.5	105.6
iC ₄ consumption.....	11.9	10.3
Selectivity.....	93.1	88.1

The data demonstrates the particular advantages of utilizing the present process in conjunction with reforming systems employing straight-run naphtha feedstocks and platinum-alumina catalysts to upgrade the isoparaffin-rich feeds obtained from the reformat. The catalyst oil produced in the two runs was only 4.7 and 7.0 weight percent.

EXAMPLE III

Five hundred and five grams of a boron trifluoride saturated solution of 50% phosphoric acid was charged to a 1-gallon stirred autoclave. The temperature was raised approximately 250° F., and 815 ml. (513 g.) of a mixture of 50 weight percent isobutane and 50 weight percent of an isoparaffinic feedstock consisting of mainly C₈ and C₉ isoparaffins was pressured into the reactor by means of a calibrated blowcase. The reactor was then pressured up to approximately 1000 p.s.i.g. and allowed to stir for two hours after which stirring was stopped, and the reactor was cooled. The contents of the reactor were drained into a room temperature trap, which was in reality a separatory funnel. The room temperature trap was connected to a series of four cold traps where condensable gases were collected. After the catalyst was collected in the room temperature trap it was drained and stored in a tared stoppered bottle. The hydrocarbon in the room temperature trap was collected and weighed. The hydrocarbon present in each of the four cold traps was also weighed. The total hydrocarbon weight (476 g.) showed a weight percent recovery of 92.8% (excluding catalyst oil).

The catalyst was decomposed by first heating to 250° F. to remove excess boron trifluoride, followed by dilution of five times its volume with water. Ether extraction of this aqueous material and subsequent removal of this ether by distillation gave 26 g. (5.1 weight percent) of catalyst oil. This brought the total recovery to 97.9 weight percent.

The hydrocarbon products (excluding catalyst oil) were combined and analyzed by vapor phase chromatography. Correcting for the isobutane charged the product distribution based upon a 92.8 weight percent recovery of total product is as follows:

Product:	Weight percent
C ₃	6.5
C ₄	—9.8
C ₅	43.7
C ₆	16.5
C ₇	7.4
i-C ₈	4.6
n-C ₈	13.0
i-C ₉	2.4
n-C ₉	1.3

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EXAMPLE IV

The raffinate feedstock of Example II was disproportionated in the presence of isobutane and 85% H₃PO₄/BF₃ according to the method of Example I but under the conditions shown in Table III below. The results are also shown in Table III.

Table III

Run No.....	22.
Catalyst.....	85% H ₃ PO ₄ /BF ₃ .
i-C ₄ /total H'C wt. ratio.....	49.6.
Catalyst wt., g.....	500.
Catalyst wt. gain.....	82.
Catalyst/total H'C wt. ratio.....	1.
Temperature, ° F.....	253.
Pressure, p.s.i.g.	480.
Products:	
Wt. percent rec.	94.8.
Catalyst oil, g.....	
Total wt. percent rec.	
i-C ₄ consumption.....	3.2.
Product distribution by V.P.C.:	
C ₃	1.7.
C ₄	48.0.
C ₅	16.0.
C ₆	5.2.
C ₇	2.8.
i-C ₈	8.3.
n-C ₈	8.1.
i-C ₉	8.7.
n-C ₉	1.2.

We claim:

1. In a method of converting low octane paraffinic feedstocks, the step comprising contacting a hydrocarbon feedstock consisting essentially of isoparaffinic hydrocarbons of 6–12 carbon atoms and isobutane with a catalytic amount of phosphoric acid-boron trifluoride catalyst in a reaction zone at a temperature of about 30 to 350° F. and having a boron trifluoride partial pressure of about 100 to 5000 p.s.i.g. and sufficient to maintain the hydrocarbon mixture at least partially in the liquid state, the weight ratio of said feedstock to isobutane being about 0.1 to 10:1, to obtain a hydrocarbon product of increased octane number rating boiling in the gasoline range.

2. In a method of converting low octane paraffinic feedstocks, the step comprising contacting a hydrocarbon feedstock consisting essentially of isoparaffinic hydrocarbons of C₆ to C₁₂ carbon atoms and isobutane with phosphoric acid-boron trifluoride catalyst in a reaction zone at a temperature of from 200 to 275° F. and having a boron trifluoride partial pressure of about 600 to 1200 p.s.i.g. and sufficient to maintain the hydrocarbon mixture at least partially in the liquid state, the weight ratio of said feedstock to isobutane being about 0.7 to 2:1, the weight ratio of total hydrocarbon to phosphoric acid catalyst being about 0.3 to 2:1 to obtain hydrocarbon product of increased octane number boiling in the gasoline range.

3. In a method of converting a hydrocarbon fraction boiling in the gasoline range, the steps comprising reforming said hydrocarbon by contact with a platinum metal-alumina catalyst in the presence of free hydrogen at a temperature of about 750–1000° F. to provide a product of increased octane value boiling in the gasoline range, separating from this product a hydrocarbon feedstock consisting essentially of isoparaffinic hydrocarbons boiling primarily in the C₆–C₁₂ range, contacting said isoparaffinic feedstock and isobutane with a catalytic amount of phosphoric acid-boron trifluoride catalyst in a reaction zone at a temperature of about 30 to 350° F. and having a boron trifluoride partial pressure of about 100 to 5000 p.s.i.g. and sufficient to maintain the hydrocarbon mixture at least partially in the liquid state, the weight ratio of said feedstock to isobutane being about 0.1 to 10:1, to obtain a hydrocarbon product of increased octane number rating boiling in the gasoline range.

4. In a method of converting a hydrocarbon fraction boiling in the gasoline range, the steps comprising reforming said hydrocarbon by contact with a platinum metal-alumina catalyst in the presence of free hydrogen at a temperature of about 750-1000° F. to provide a product of increased octane value boiling in the gasoline range, separating from this product a hydrocarbon feedstock consisting essentially of isoparaffinic hydrocarbons boiling primarily in the C₆-C₁₂ range, contacting said hydrocarbon feedstock consisting essentially of isoparaffinic hydrocarbons of C₆ to C₁₂ carbon atoms and isobutane with phosphoric acid-boron trifluoride catalyst in a reaction zone at a temperature of from 200 to 275° F. and having a boron trifluoride partial pressure of about 600 to 1200 p.s.i.g. and sufficient to maintain the hydrocarbon mixture at least partially in the liquid state, the weight ratio of said feedstock to isobutane being about 0.7 to 2:1, the weight ratio of total hydrocarbon to phosphoric acid catalyst being

about 0.3 to 2:1, to obtain a hydrocarbon product of increased octane number boiling in the gasoline range.

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