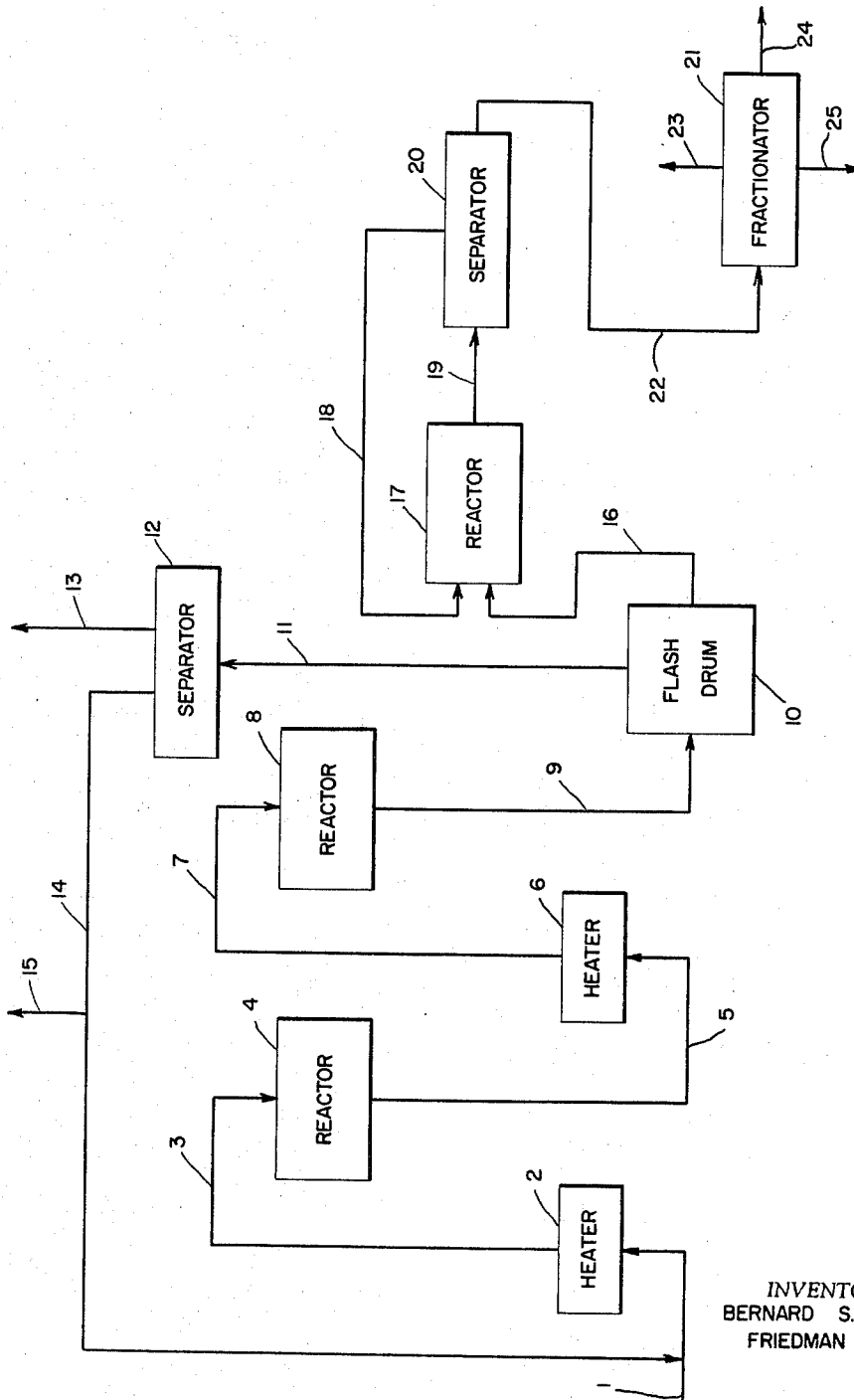


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METHOD OF PRODUCING A HIGH OCTANE GASOLINE
BY REFORMING A NAPHTHA IN TWO STAGES
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METHOD OF PRODUCING A HIGH OCTANE GASOLINE BY REFORMING A NAPHTHA IN TWO STAGES

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This invention relates to a method for the conversion of hydrocarbon fractions boiling in the motor fuel range to obtain products of higher octane value. More particularly, the invention is concerned with the conversion of straight run petroleum fractions boiling in the motor or spark-ignition engine fuel range to obtain good yields of higher octane gasoline by the use of a plurality of reaction stages employing catalysts differing in characteristics.

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 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 a high octane hydrocarbon fuel component can be obtained by employing processing methods other than or in conjunction with the platinum metal-alumina catalyst reforming operation.

In the present invention I have devised a highly attractive method for obtaining high octane fuels for spark-ignition engines which involves the use of separate reaction zones in which are employed catalysts of different properties. In this method a straight run gasoline or naphtha boiling range hydrocarbon is contacted with a platinum metal-alumina catalyst in the presence of free

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hydrogen under conditions which provide a substantial increase in the octane number of the petroleum hydrocarbon material. The resulting reformate is then treated with a catalyst comprising hydrogen fluoride and boron trifluoride to afford another substantial increase in the octane quality. In the treatment using the platinum metal catalyst the reformate obtained preferably has an octane quality in the range of about 75 to 95 RON neat and will usually not rate more than about 100 RON neat. This octane quality is determined, among other things, by the severity of the catalytic reforming operation which affects reactions such as isomerization, dehydrocyclization, hydrocracking and dehydrogenation. In this system at least a substantial amount of the naphthenes present in the straight run feed are converted to aromatics through the latter reaction.

The over-all hydrocarbon material which is charged to the hydrogen fluoride-boron trifluoride reaction system boils in the motor fuel range and is composed of about 20 to 80, preferably about 30 to 60, weight percent of aromatics. Usually the reformate from the platinum metal-alumina catalyst system contains about 30 to 60 weight percent of such constituents and this entire product or any fraction thereof which provides an over-all hydrocarbon feed containing the desired amount of aromatics can be treated with the hydrogen fluoride-boron trifluoride catalyst. The boiling range of this rather mixed reformate fraction will generally extend over at least about 100° F. preferably at least about 200° F. A product unusually high in aromatic constituents can be made by obtaining and then charging a reformate directly from the platinum metal catalyst reaction zone which is relatively rich in aromatics, but more likely such products will be made available through the selection of particular fractions of the reformate, or by recycle of aromatic constituents alone or with the hydrogen fluoride-boron trifluoride catalyst from this reaction system. In designating amounts of aromatics I refer to the value obtained by the Fluorescence Indicator method commonly known as the F.I.A. method involving chromatography on silica gel.

The hydrocarbon feed stocks charged to the reaction system containing the platinum metal-alumina catalyst are primarily the straight run petroleum fractions boiling in the naphtha range, for instance in the range from about 200 to 450° F., but somewhat higher or lower boiling constituents can be included if desired. Preferably, the feed stock boils in the range of about 225 to 400° F. Although the hydrocarbons passing to the platinum metal-alumina catalyst reaction system are composed of predominantly straight run naphtha material, minor amounts of additional components can be included such as olefins, thermal and catalytically cracked stocks, recycled reformate and fractions of these cracked and reformed materials. 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.

These catalysts can be made by a number of procedures but a particularly effective catalyst is one in which the alumina is obtained through calcination of an alumina hydrate containing at least about 65 weight percent of trihydrate and about 5 to 35 weight percent of alumina monohydrate and/or amorphous alumina forms, and advantageously having a surface area of about 350 to about 550 square meters per gram (BET method) when in the virgin state. The minor amount of platinum metal in the catalyst is usually present in finely divided form and is not detectable by X-ray diffraction techniques. Also, these catalysts are advantageously prepared to afford about 0.10 to 0.5, preferably about 0.15 to 0.3 cc./gram of their pore volume in pores of about 100 to 1000 Angstrom units in size. Application Serial No. 489,726, filed February 21, 1955, describes the preparation of such catalysts. If desired, the catalyst can contain minor amounts of additional materials, for instance promoting components particularly those acidic in nature, such as silica and fluoride. Such promoting components are usually less than 10 weight percent of the final calcined catalyst.

The platinum metal-alumina catalyst can be employed in any type of reaction system desired, for instance moving or fluidized bed, regenerative or non-regenerative, etc., but advantageously the catalyst is disposed as a fixed bed. In the latter type of operation the size of commercial units is such that essentially adiabatic reaction systems must be employed and in view of this and the endothermic nature of the reforming operation the catalyst is placed in fixed beds in a plurality of reactors, each of which is preceded by means for heating its charge. In fixed bed operations the catalyst is in macrosized form, that is particles generally at least about $\frac{1}{16}$ " in length and diameter and preferably not exceeding about $\frac{3}{8}$ " in diameter. Particularly when such particles are provided by extrusion, their length may be up to about 1" or more. If the platinum metal-alumina catalyst reforming system be of the regenerative type it can be arranged so that the catalyst of all of the reactors can be regenerated simultaneously or individually. Other variations in the platinum metal catalyst reaction system can be made according to the desires of the operator.

The essential feed to my hydrogen fluoride-boron trifluoride catalyst system contains a substantial part or all of the liquid reformat from the platinum metal catalyst operation and as noted above the over-all hydrocarbon feed includes from about 20 to 80 weight percent of aromatic constituents, preferably about 30 to 60 weight percent. The feed stock boils in the motor fuel range, for instance up to about 425° F., although heavier constituents can be included. Preferably, the boiling range of the feed stock lies within the range of about 225 to 400° F. Recycled materials such as aromatics from the hydrogen fluoride-boron trifluoride reaction system can be returned to the system or various materials such as straight run naphthas, thermal or catalytically cracked gasolines and their fractions can be added. I prefer that the charge to the hydrogen fluoride-boron trifluoride reaction zone be composed of at least about 50 weight percent of reformat from the platinum metal-alumina catalyst reaction system or a fraction thereof boiling over a range of at least about 100° F., preferably over a range of at least about 200° F. The hydrogen fluoride-boron trifluoride catalyst can be employed in the substantial absence of added free hydrogen. However, such a gas can be employed to minimize sludge and heavy oil formation. When using hydrogen I prefer about 1 to 10 moles per mole of hydrocarbon feed. Paraffins such

as propane, butane, isobutane, isopentane or pentane can be passed to the hydrogen fluoride-boron trifluoride reaction zone to minimize cracking.

In the hydrogen fluoride-boron trifluoride reaction system the conditions of treatment can vary widely depending upon factors such as feed composition, octane desired for the final product, etc. I maintain the catalyst essentially in the liquid state even though when this is done it is quite likely that a portion of the boron trifluoride would also be present as vapor. Thus the pressure maintained must be sufficient to provide essentially liquid phase reaction conditions as determined by the vapor pressure of the hydrogen fluoride, boron trifluoride, the reactants and other materials such as hydrogen and reaction products present. Generally, the pressure will be above atmospheric in maintaining the liquid phase reaction. The reaction temperature and time are interdependent factors with a lesser time required to provide products of given octane as the temperature increases. The reaction temperature will usually be in the range of about 50 to 300° F., preferably at least about 150° F., with the time required ranging from about $\frac{1}{2}$ minute to 5 hours, preferably about 10 minutes to $1\frac{1}{2}$ hours. Times longer than 5 hours can be employed; however, no particular advantage has been derived thereby which overcomes the obvious economic disadvantages. In the reaction zone at least about 0.75, preferably at least about 1.0, mole of boron trifluoride is provided in the liquid phase per mole of aromatics present and due to economic considerations this ratio will usually not exceed about 5 to 1 or even about 2 to 1. In general I employ at least about 0.5, preferably about 1 to 10, moles of hydrogen fluoride per mole of aromatic constituent. These catalytic components can be added separately but preferably they are introduced into the reaction zone in admixture. The hydrogen fluoride-boron trifluoride reaction system is usually conducted essentially in the absence of water to avoid having to increase the amount of boron trifluoride, but frequently there are minor amounts of water present such as those derived through the use of commercially available hydrogen fluoride and boron trifluoride. The pressure in this reaction system is sufficient to maintain the liquid phase reaction and frequently is in the range of about 400 to 1500 p.s.i.g.

The hydrocarbon product from the hydrogen fluoride-boron trifluoride reaction zone can be separated in a number of ways. Should agitation of the reaction mixture be stopped it will generally separate into two phases in the reactor or in any other vessel into which it is transferred as in a continuous, semi-continuous or batch operation. Regardless of where the phase separation takes place or if the formation of these phases is prevented by continuous agitation, the catalyst and hydrocarbon materials can be separated by any desired procedure. For instance, the over-all product containing both the catalyst and hydrocarbon can be water washed to remove the former. Preferably, however, in this type of system I reduce the pressure maintained on the reaction product to allow the boron trifluoride and then the hydrogen fluoride to distill or be flashed and this operation is followed by water washing to remove remaining catalyst. Alternatively, only the boron trifluoride might be distilled which would permit the hydrogen fluoride to separate from the hydrocarbon by gravity and the hydrocarbon layer could then be decanted and water washed.

In another type of system the reaction mixture could be allowed to separate into a lower layer of catalyst containing aromatics which can be recycled to the reaction system in whole or in part. The upper hydrocarbon layer formed could be freed from catalyst by distillation and/or washing with water or passed through a column of basic ion exchange resin or other solid adsorbent such as charcoal. In this system aromatics in the catalyst layer could be separated as by distillation of the catalyst,

and the aromatics might then be combined with the hydrocarbons of the upper layer to provide a higher octane product. Small traces of fluoride remaining in the hydrocarbon material can be removed as by passage over aluminum or alumina at 200 to 400° F. Various drying procedures could be employed to separate water from the hydrocarbon materials and such materials could be stabilized, for instance by the removal of C₄'s and lighter constituents.

In the drawing I have illustrated a simplified flow sheet of an operation conducted in accordance with my method.

In this system straight run naphtha is charged by way of line 1 to heater 2 and then through line 3 to an initial reactor 4 which contains a fixed bed of platinum-alumina catalyst. The effluent from reactor 4 is passed by way of line 5 to heater 6 and then through line 7 to a second reactor 8 containing platinum-alumina catalyst. The platinum-alumina catalyst reaction section is of the adiabatic type and more than two reactors can be provided if desired and in fact usually at least three catalyst beds in separate reactors will be employed with each reactor having associated therewith a feed preheater.

The reformat from reactor 8 is passed by way of line 9 to atmospheric flash drum 10 which separates C₄'s and lighter materials which are passed through line 11 to separator 12. The separator provides for removal of C₂ to C₄ hydrocarbon constituents through line 13 and hydrogen and methane are passed by way of line 14 to line 1. Excess hydrogen and methane can be removed from line 14 by way of line 15.

The liquid hydrocarbon reformat from flash drum 10 is conveyed by way of line 16 to reactor 17 where it is contacted with the hydrogen fluoride-boron trifluoride catalyst entering by way of line 18. The reaction mixture is continuously withdrawn from reactor 17 and passed by way of line 19 to separation section 20. The hydrogen fluoride-boron trifluoride catalyst separated from the hydrocarbon product can be recycled by way of line 18 to reactor 17. The liquid hydrocarbon product obtained from separation section 20 is conveyed to fractionator 21 by way of line 22 which separates C₄'s and lighter materials overhead by way of line 23, motor fuel boiling range products by way of line 24, and heavier hydrocarbons as bottoms through line 25.

The following specific examples will serve to illustrate the present invention; however, they are not to be considered limiting.

Example I

A straight run naphtha is obtained by distillation from crude oil and the naphtha typically has an ASTM distillation boiling range of about 195 to 380° F. and a RON (neat) of about 44.8. 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 application Serial No. 489,726, listed above. The inlet temperatures of the feed to the three catalyst beds are 946, 936 and 926° F., respectively, 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 obtained by recycle from the third reactor effluent stream. The molar ratio of hydrogen-rich recycle gas to hydrocarbon feed is approximately 7.3 to 1.0 while the over-all space velocity is about 2.26 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. Inspection on the resulting reformat is as follows:

ASTM distillation, ° F.:

I.B.P. _____	95.
50% _____	241.
90% _____	327.
E.P. _____	390.
RON _____	90.5 (neat); 98.0 (3 cc. TEL added/gal.).
R.V.P. _____	9.4 lbs.
Aromatics _____	49.9% by F.I.A.
Olefins _____	2.5% by F.I.A.

418 grams of the reformat is distilled to obtain 91.5 weight percent of C₅+ gasoline and 4.67 weight percent of butanes (iso+normal). Inspection on the stabilized gasoline fraction is as follows:

ASTM distillation, ° F.:

I.B.P. _____	121.
50% _____	243.
90% _____	318.
E.P. _____	353.
RON _____	88.7 (neat); 97.5 (3 cc. TEL added/gal.).
R.V.P. _____	4.2 lbs.
Aromatics _____	50.8%.
Olefins _____	1.3%.

300 grams of the 95°-390° F. reformat is placed in a cool 1750 ml. stainless steel Magnedash bomb having tapered walls to give maximum thickness in the bottom half of the bomb. To the cool bomb is added 10 moles of hydrogen fluoride. The bomb is sealed and charged with 6.4 moles of boron trifluoride by pressuring from a 2-liter cylinder fitted with a pressure gauge. The amount of boron trifluoride introduced is estimated by interpolation from the data of Kilpatrick and Luborsky, J.A.C.S. 76, 5866 (1954). While stirring the contents of the bomb it is heated for 65 minutes to reach 150° F. This temperature is held for 30 minutes and the pressure reaches a maximum of 880 p.s.i.g. The contents of the bomb are discharged through the bottom draw-off into a mixture of ice and water. Gases are conducted through a Dry-Ice cooling trap, safety trap, water scrubber, gas sampler and wet test meter. The hydrocarbon layer is separated from the ice water and the former is washed three times with separate 500 cc. portions of water. The washed hydrocarbon is dried by contact with potassium carbonate. The products obtained are 271.5 grams of liquid hydrocarbon, 10.5 grams of condensable gas and 3.2 liters (STP) of dry gas. The condensable gas and liquid are then combined and distilled through a 12" glass helices, vacuum-jacketed distillation column to separate 4.18 weight percent of C₃-C₄ wet gas, 79.3 weight percent of initial to 400° F. overhead gasoline and 7.17 weight percent of a still residue boiling above 400° F. The yield of gasoline when corrected for handling and mechanical losses is about 87.8 weight percent and since the gasoline fraction has a 378° F. end point the yield would be increased by distilling to 435° F. to obtain the usual nominal 410° F. end point gasoline. Inspection of the gasoline fraction is as follows:

ASTM distillation, ° F.:

I.B.P. _____	116.
50% _____	228.
90% _____	346.
E.P. _____	378.
RON _____	93.6 (neat), 101 (3 cc. TEL added/gal.).
Aromatics _____	49.5%.
Olefins _____	0.4%.

Thus by treating the reformat from the platinum-alumina catalyst system with the hydrogen fluoride-boron trifluoride catalyst the clear research octane number of the

resulting stabilized gasoline was increased by 4.9 numbers and the higher octane product showed a good lead susceptibility.

Example II

426 grams of the reformat produced in the platinum-alumina catalyst system of Example I is placed in the magnedash bomb described in Example I. To the cool bomb is added 5.37 moles of hydrogen fluoride. The bomb is sealed and charged with 3.15 moles of boron trifluoride by pressuring as in Example I. While stirring the contents of the bomb it is heated for 97 minutes to reach 245° F. This temperature is held for 30 minutes and the pressure reaches a maximum of 975 p.s.i.g. The bomb contents are then discharged and worked up as in Example I. The products obtained are 401.0 grams of liquid hydrocarbon, 8.0 grams of condensable gas and 3.07 liters (STP) of dry gas. The condensable gas and liquid are then combined and distilled through a 12" glass helices, vacuum-jacketed distillation column to separate 10.55 weight percent of C₃-C₄ wet gas, 73.1 weight percent of initial to 400° F. overhead gasoline and 8.46 weight percent of a still residue boiling above 400° F. The yield of gasoline when corrected for handling and mechanical losses is about 79.4 weight percent and since the gasoline fraction has a 370° F. end point the yield would be increased by distilling to 435° F. to obtain the usual nominal 410° F. end point gasoline. Inspection of the gasoline fraction is as follows:

ASTM distillation, ° F.:

I.B.P.	113.
50%	237.
90%	334.
E.P.	370.
RON	95.0 (neat), 100.5 (3 ct. TEL added/gal.).
Aromatics	49.6%
Olefins	0.5%
R.V.P.	4.95 lbs.

Thus by treating the reformat from the platinum-alumina catalyst system with the hydrogen fluoride-boron trifluoride catalyst the clear research octane number of the resulting stabilized gasoline was increased by 6.3 numbers and the higher octane product showed a good lead susceptibility.

Example III

5.4 moles of hydrogen fluoride is added to the Magnedash bomb described in Example I. The bomb is sealed and charged with 3.2 moles of boron trifluoride by pressuring from a cylinder as in Example I. While stirring, the bomb is heated to a temperature of 250° F. and 380 grams of the reformat obtained in the platinum-alumina catalyst operation of Example I is charged by forcing the hydrocarbon feed from a charger under nitrogen pressure. The 250° F. temperature is then held for 22 minutes and the pressure reaches a maximum of 1110 p.s.i.g. The bomb contents are discharged through the bottom draw-off into a mixture of ice and water and worked up as in Example I. The products are 352.0 grams of liquid hydrocarbon, 13.0 grams of condensable gas and 3.95 liters (STP) of dry gas. The condensable gas and liquid are then combined and distilled through a 12" glass helices, vacuum-jacketed distillation column to separate 9.88 weight per cent of C₃-C₄ wet gas, 73.18 weight percent of initial to 400° F. overhead gasoline and 9.74 weight percent of still residue boiling over 400° F. Correcting for mechanical and distillation losses the yield of initial to 400° F. gasoline is about 79 weight percent and this could be increased by taking the distilla-

tion overhead to 435° F. to secure the usual nominal 410° F. end point gasoline. Inspection of the gasoline fraction is as follows:

ASTM distillation, ° F.:

I.B.P.	111.
50%	240.
90%	330.
E.P.	370.
RON	95.5 (neat).
R.V.P.	5.65 lbs.
Aromatics	55.2%
Olefins	0.4%

These data show the substantial increase in octane of the stabilized gasoline afforded by the operation using the hydrogen fluoride-boron trifluoride catalyst.

I claim:

1. In a method for the conversion of a straight run hydrocarbon fraction boiling in the motor fuel range, the steps comprising contacting said hydrocarbon fraction with a platinum metal-alumina catalyst in the presence of free hydrogen at a temperature of about 750 to 1000° F. and a pressure of about 50 to 1000 p.s.i.g. to provide a product boiling in the motor fuel range of increased octane value, separating a resulting hydrocarbon liquid product boiling over a range of at least about 100° F., contacting with a catalyst consisting essentially of hydrogen fluoride and boron trifluoride, a hydrocarbon material containing a substantial amount of said separated product, said hydrocarbon material boiling in the motor fuel range and containing about 20 to 80 weight percent of aromatics at a temperature of about 50 to 300° F. and a pressure sufficient to maintain the liquid phase to provide a further increase in the octane quality of the product boiling in the motor fuel range, the contacted hydrogen fluoride, boron trifluoride and hydrocarbon including at least about 0.75 mole of boron trifluoride and about 0.5 to 10 moles of hydrogen fluoride per mole of aromatic in the hydrocarbon and separating a motor fuel boiling range hydrocarbon of high octane quality.

2. In a method for the conversion of a straight run hydrocarbon fraction boiling in the motor fuel range, the steps comprising contacting said hydrocarbon fraction with a platinum-alumina catalyst in the presence of free hydrogen at a temperature of about 825 to 975° F. and a pressure of about 150 to 500 p.s.i.g. to provide a product boiling in the motor fuel range of increased octane value, separating a resulting hydrocarbon liquid product boiling over a range of at least about 200° F. and containing about 30 to 60 weight percent of aromatics, contacting said separated liquid product with a catalyst consisting essentially of hydrogen fluoride and boron trifluoride at a temperature of about 150 to 300° F. and a pressure of about 400 to 1500 p.s.i.g. and sufficient to maintain the liquid phase to provide a further increase in the octane quality of the product boiling in the motor fuel range, the contacted hydrogen fluoride, boron trifluoride and hydrocarbon including about 1 to 2 moles of boron trifluoride and about 1 to 10 moles of hydrogen fluoride per mole of aromatic in the hydrocarbon and separating a motor fuel boiling range hydrocarbon of high octane quality.

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