

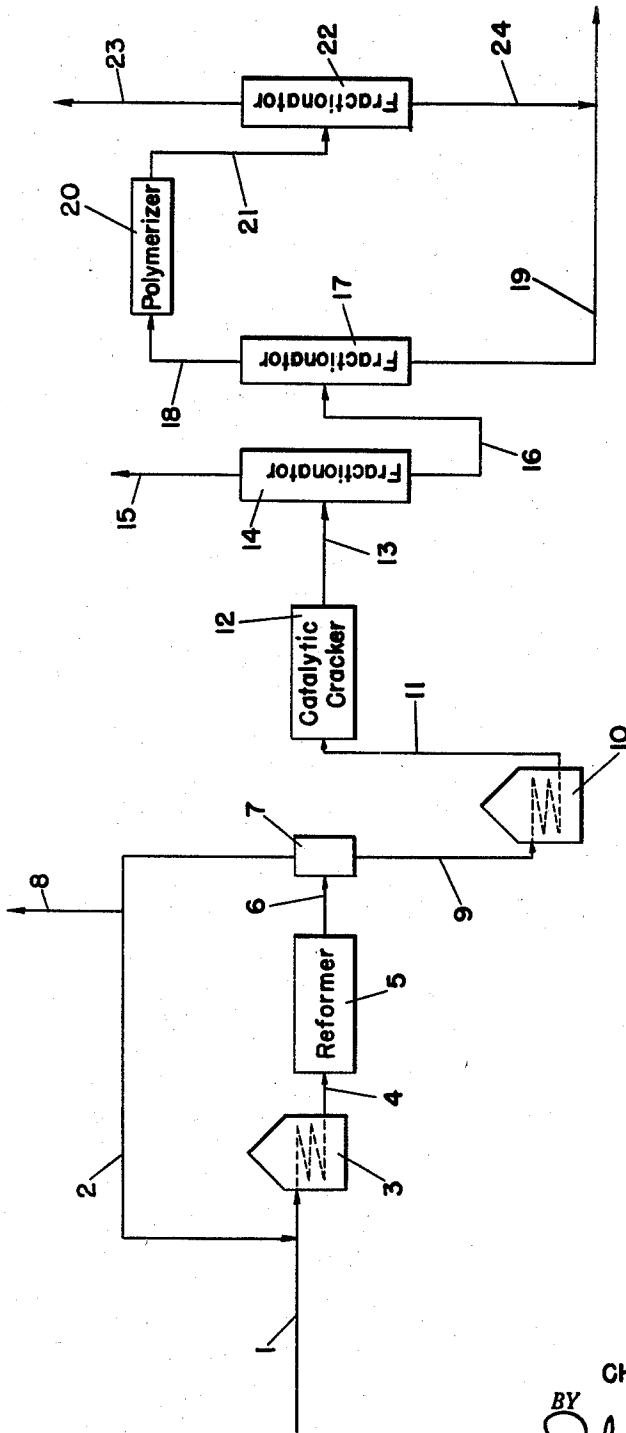
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HIGH OCTANE GASOLINE MANUFACTURE

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HIGH OCTANE GASOLINE MANUFACTURE

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This invention relates to the production of high octane gasolines, and more particularly to a combination process for the treatment of a straight-run naphtha wherein the naphtha is subjected first to a reforming operation in the presence of a dual-function dehydrogenation-isomerization catalyst, and is then catalytically cracked to convert low octane paraffins to normally liquid higher octane compounds or to normally gaseous olefins capable of being polymerized to a high octane gasoline fraction.

Conventional catalytic reforming of a straight-run petroleum fraction in the gasoline boiling range, having an initial octane number below 60, will yield a product having an octane number in the range of 80 to 90, which can be upped to about 88 to 95 by the addition of small amounts of tetraethyl lead. While gasoline of this quality will satisfy most present-day automobiles, the trend is toward higher compression motors, which have octane demands approaching 100 O.N. It is therefore necessary that processes be developed which will enable a petroleum refiner to produce gasoline of this quality in high yields. The principal object of this invention is to provide such a process.

In accordance with the present invention, a straight-run gasoline boiling over the full gasoline boiling range, say from about 90° F. to about 400° F., is subjected to the action of a dual-function reforming catalyst at a temperature of from about 850° F. to about 975° F.; at pressures of from about 200 p.s.i.g. to about 600 p.s.i.g.; and in the presence of from about 1 to about 10 mols of added hydrogen per mol of hydrocarbon. The dual-function catalyst, which is essential in the process, is preferably platinum deposited on a base which has high temperature acidic characteristics, such as alumina containing from about 0.3 to about 3 percent combined fluorine. Other acidic bases which are suitable for use in practicing my invention include synthetic silica-alumina, boria-alumina and acid treated naturally occurring clays. Under the foregoing conditions, the platinum component of the catalyst promotes dehydrogenation of naphthenes to the corresponding aromatics, while the acidic component among other things promotes isomerization of paraffins to more highly branched structures. If the catalyst contains no acidic component as in the case where the catalyst comprises platinum or VI group metal oxides deposited on alumina alone, the paraffins contained in the feed will be subjected to some hydrocracking, but the majority will pass through the reforming step untouched, and will appear in the liquid product as straight-chain or only moderately branched compounds, which, for reasons which will be hereinafter pointed out are undesirable.

The liquid product from the reforming step is then passed to a cracking zone in which it is subjected to the action of a cracking catalyst such as synthetic silica-alumina, bauxite, or certain naturally occurring clays. Temperature in the cracking zone should be from about 850° F. to 975° F., and the space velocity (volume of feed/volume of reactor/hr.) should be from about

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0.5 to 2. It has been found that under these conditions the branched chain paraffins will be rather easily cracked to low-boiling olefins, such as propylene, n-butylenes, and isobutylene, whereas the aromatics, being much more refractory, will pass through unchanged, except for removing some of the alkyl side chains of three or more carbon atoms. I have found that branched chain paraffins are catalytically cracked with considerably less difficulty than straight chain paraffins, and that the yields of polymerizable gaseous olefins are much higher, under the same operating conditions, if the feed to the cracking zone contains a large amount of branched chain paraffins than if the paraffin content is largely straight chain as would be the case when a non-acidic catalyst base is used in the reforming step. Moreover, the C₄ olefins formed will comprise considerably more isobutylene, which forms a more valuable feed to a polymerizer than the normal butylenes. For this reason, as has been stated above, isomerization of the feed paraffins to more highly branched structures by the use of an acidic support for the platinum catalyst in the reforming step, goes to the essence of the present invention.

The products of the cracking step are then fractionated to take overhead a C₄ and lower fraction, and a C₅+ fraction as bottoms. Since a good proportion of the paraffins in the feed to the cracking zone are cracked therein to C₃ and C₄ hydrocarbons, while the aromatic content is virtually untouched, the concentration of aromatics in this product will be considerably higher than in the feed, with accompanying increase in octane number. A higher octane number is also favored by the catalytic cracking of higher-boiling, low octane number, paraffins to lower-boiling C₅+ branched chain paraffins and olefins of increased octane number.

The C₃ and C₄ fraction taken off as overhead in the fractionation may then be polymerized in known fashion to make a high octane number gasoline, which is then combined with the aromatic bottom fraction, and with an appropriate amount of extraneous butanes or other blending stocks to form a finished high octane gasoline of balanced volatility.

In order that those skilled in the art may more fully understand the nature of my invention and the method of carrying it out, it will be more fully described in connection with the accompanying drawing, which is a diagrammatic flow sheet of the process, certain process equipment, such as pumps, valves, etc., being omitted for the sake of simplicity and clarity.

As may be observed from the drawing, a feed stock, which may be a straight-run naphtha boiling from 90° F. to about 400° F. or a selected fraction thereof, is taken from storage through line 1, and is mixed with a recycle hydrogen stream introduced through line 2. The mixture is then passed through a furnace 3 in which it is heated to a temperature of from about 850° F. to about 975° F., preferably from about 900° F. to about 925° F. From furnace 3 the mixture is taken through line 4, at a pressure of from about 200 p.s.i.g. to about 600 p.s.i.g. (preferably about 400 p.s.i.g.) and is passed to a reforming zone 5, which is packed with a catalyst comprising platinum supported on a fluorine-containing alumina. The method for preparing such a catalyst is fully described in U.S. Patent 2,479,110 to Haensel, so that further description of the catalyst is deemed unnecessary here. Under the conditions prevailing in the reforming zone, the cyclohexanes in the feed will be dehydrogenated to the corresponding aromatics, the alkyl cyclopentanes will be largely isomerized to cyclohexanes and dehydrogenated to aromatics, and a large part of the paraffins will be isomerized to more highly branched structures. Since only moderately elevated pressures are employed, hydro-

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cracking is minimized, thus assuring a high yield of liquid product.

Reaction products are removed from reforming zone 5 through line 6 and are passed to separator 7 from which hydrogen-containing gases are removed overhead. A sufficient amount of this gas is recycled to the process through line 2 to maintain the mol ratio of hydrogen to hydrocarbon in the feed to the reforming zone at a value of from about 1:1 to about 10:1; excess hydrogen produced in the process being vented from the system through line 8. The balance of the reformate, which will have an octane number of between about 80 and 90, depending on the initial octane number of the feed and upon the severity of the operating conditions in reforming zone 5, is then taken through line 9 to furnace 10, in which it is heated to a temperature of from about 850° F. to about 975° F., and preferably to about 900° F., and is then passed through line 11 to a catalytic cracking zone 12.

The cracking process utilized in catalytic cracking zone 12 may be of any conventional type, such as fixed bed, moving bed, or fluid, and will, of course, include facilities for the regeneration of catalyst contained therein. The catalyst may be any conventional cracking catalyst, such as a synthetic silica-alumina gel, bauxite, or naturally occurring clays. The feed to cracking zone 12 is admitted thereto at a rate such that its average residence time therein is sufficient to permit the cracking of a large part of the paraffin content to low-boiling olefins, while avoiding any appreciable demethylation of aromatics. Normally the space velocity (liquid volume of feed/volume of catalyst/hour) will be from about 0.5 to about 2.

Cracked products are withdrawn from cracking zone 12 through line 13 and are passed to fractionator 14, from which ethane and lower-boiling hydrocarbons are drawn off overhead through line 15 for use as fuel or for such other disposal as may be desired. Bottoms from fractionator 14 are withdrawn through line 16 and are passed to fractionator 17 from which a C₃-C₄ fraction containing a high percentage of olefins is removed overhead through line 18. A C₅ and higher hydrocarbon fraction, which, due to the removal of paraffins by selective cracking is richer in aromatics than the feed to cracking zone 12, is removed from fractionator 17 through line 19. This fraction will have an octane number (F-1 clear) of from 95 to 100 or over depending on the severity of conditions in the cracking zone.

The C₃-C₄ fraction removed from fractionator 17 is passed to a polymerization zone 20 in which it is contacted with a polymerization catalyst such as sulphuric or phosphoric acid at standard polymerization conditions well known to the art. Reaction products from polymerization zone 20 are passed through line 21 to fractionator 22, from which unreacted normally gaseous hydrocarbons are withdrawn overhead through line 23. A high octane polymer gasoline is withdrawn from fractionator 22 through line 24 and is combined with the bottoms from fractionator 17. If desired, of course, the polymer gasoline may, instead of being combined with the aromatic fraction, be used for blending with other lower octane number refinery stocks. Similarly, the aromatic fraction is useful as gasoline per se, or for blending with other stocks.

As may be observed from the foregoing, I have devised a process for the production of high octane gasoline from low octane straight-run naphtha in which there is a minimum loss to gaseous hydrocarbons. Since conditions in reforming zone 5 are such as to minimize hydrocracking, the loss in this step will be chiefly hydrogen produced in the dehydrogenation of naphthenes, and since conditions in catalytic cracking zone 12 are such as to minimize demethylation of aromatics, there will be very little loss to C₂ and lower hydrocarbons in this step, since the normally gaseous products from catalytic cracking are chiefly C₃ and C₄ hydrocarbons. The C₃ and C₄ hydro-

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carbons produced in the cracking step are largely olefinic so that they may be converted into polymer gasoline to recover an ultimate high yield of high octane gasoline.

While my new process may bear some superficial resemblance to some of the processes of the prior art, upon closer examination it will be apparent that it is clearly distinguishable from the most pertinent art, and that superior results are obtained by proceeding in accordance therewith. For example, Voorhies in U.S. Patent 2,361,138, hydroforms a straight-run naphtha, and catalytically cracks that portion of the hydroformate boiling above 300° F., to recover material boiling in the aviation gasoline range, which is blended with the hydroformate boiling below 300° F. The catalyst used in the reforming step is molybdenum oxide, which does not promote paraffin isomerization. Thus Voorhies' gasoline product contains a considerable proportion of paraffins, largely straight chain or only moderately branched, boiling below 300° F. While these paraffins have a higher octane number than paraffins boiling above 300° F., they have an octane number considerably below the octane number of the isoparaffins plus the polymer gasoline in the final product made according to the present invention, and consequently the octane number of the finished gasoline will be lower.

Wetly in U.S. Patent No. 2,380,279 and Oblad in U.S. Patent No. 2,383,072 describe processes in which the higher boiling fractions of a hydroformate are catalytically cracked to dealkylate the higher-boiling aromatics to toluene. As pointed out above, when proceeding according to the present invention, in the cracking step no substantial demethylation of aromatics, with consequent losses to methane and other uncondensable gases, takes place. Furthermore, in the present process the entire reformate, rather than the higher boiling fraction thereof, is subjected to the cracking step.

In Wetly U.S. Patent No. 2,490,287, a naphtha is reformed over a molybdenum oxide catalyst, and the reformate is subjected to thermal reforming, apparently to isomerize the paraffins. While the octane number is thereby improved, only a minor concentration of the aromatics, by destruction of paraffins, is obtained, with the production of a negligible quantity of low-boiling olefins, suitable for processing into high octane polymer gasoline. Furthermore, thermal cracking makes more C₁ and C₂ hydrocarbons, which are lost to uncondensable gases, than catalytic cracking.

It will thus be seen that, while useful two step processes for the treatment of straight-run naphthas, involving reforming in one step and cracking in the other, are broadly old, my invention is an improvement over previously proposed processes. This improvement resides in the concept that by treatment of the naphtha with a dual-function dehydrogenation-isomerization catalyst in the first step of my process, it is possible to convert the paraffins in the feed to branched chain structures which are easily catalytically cracked to olefins, suitable for further processing to polymer gasoline, under conditions such that the aromatics in the feed to the cracking step are largely unconverted. Cracking of the paraffins in this manner not only produces a suitable feed stock for polymerization, but also results in an increased concentration of aromatics in the liquid product from the cracking step, with resultant very high octane number, and the combination of this product with the polymer gasoline formed in the process yields a gasoline with a yield/octane relationship superior to any of the prior art two stage processes.

It will be appreciated that while certain preferred temperatures and pressures have been set forth above, the optimum temperatures and pressures may vary somewhat, depending on the composition of the feed to each step. For example, if the feed to the reforming step is a full-boiling range naphtha the operating conditions should be somewhat more severe than when charging a

fraction having an initial boiling point of say 250° F. Similarly, optimum temperatures in the cracking step will depend to some extent on the degree of paraffin isomerization obtained in the reforming step. In general, however, the process is operable over the full extent of the wider temperature and pressure ranges given above.

The invention claimed is:

1. A process for the production of high octane gasoline which comprises passing a straight-run naphtha boiling within the gasoline boiling range to a reforming zone, therein subjecting said naphtha to the action of a dual-function dehydrogenation-isomerization catalyst at a temperature of from 850° F. to 975° F., at a pressure of from 200 p.s.i.g. to 600 p.s.i.g. and in the presence of added hydrogen, separating a normally liquid product from the effluent from the reforming zone; passing said normally liquid product to a catalytic cracking zone and subjecting it therein to the action of a cracking catalyst selected from the group consisting of synthetic silica-alumina gel, bauxite, and naturally-occurring clays, in the absence of added hydrogen, at a temperature of from 850° F. to 975° F., and at a liquid hourly space velocity of 0.5 to 2, the temperature and space rate being correlated to produce a cracking severity insufficient to substantially demethylate aromatics; recovering a second reaction product from the catalytic cracking zone, and fractionating the second reaction product to recover a C₃-C₄ frac-

tion comprising olefins, and a higher boiling fraction rich in aromatics.

2. The process according to claim 1 in which the dual-function dehydrogenation-isomerization catalyst comprises platinum deposited on alumina containing from about 0.3 to about 3.0 percent combined fluorine.

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