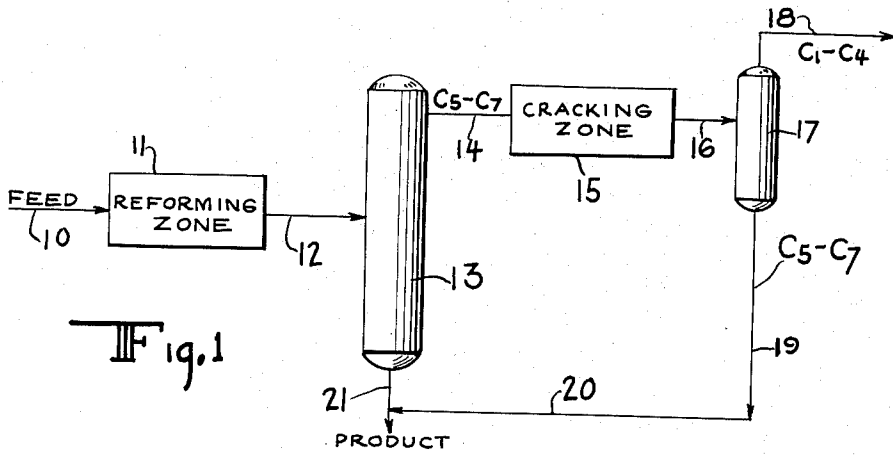
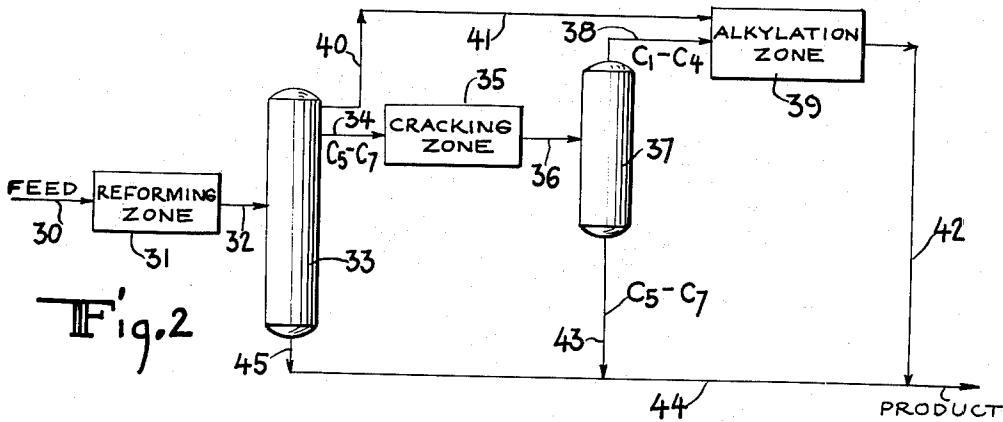
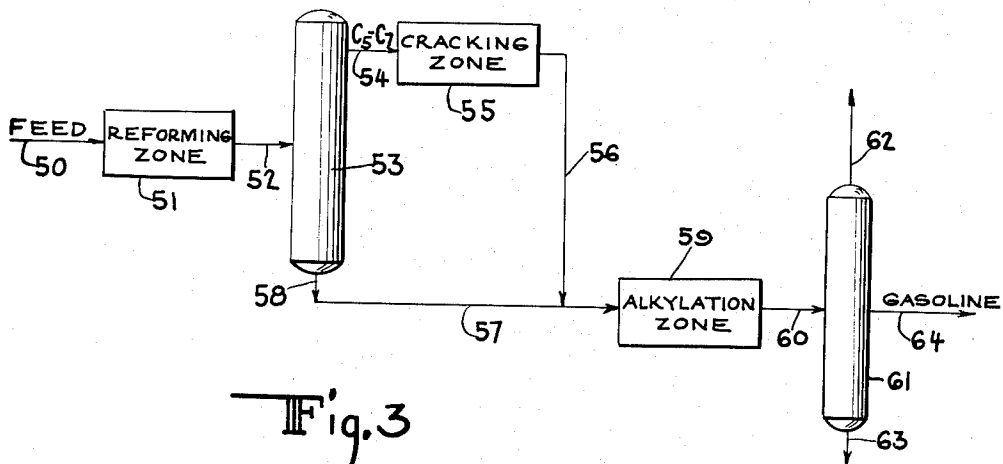


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P. B. WEISZ
UPGRADING OF NAPHTHAS
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UPGRADING OF NAPHTHAS

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This invention relates to a process for upgrading petroleum naphthas. More particularly, the present invention is directed to a process for improving the octane-number quality of a gasoline.

The octane number of a gasoline depends generally on the character and content of the various hydrocarbon components thereof. Reforming operations, wherein hydrocarbon fractions such as naphthas, gasolines and kerosenes are treated to improve the anti-knock properties thereof are well known in the petroleum industry. These fractions are composed predominately of normal and slightly branched paraffinic hydrocarbons and naphthenic hydrocarbons together with small amounts of aromatic hydrocarbons. During reforming a multitude of reactions take place including isomerization, aromatization, dehydrogenation, cyclization, etc. to yield a product having an increased content of aromatics and highly-branched paraffins. Thus in reforming, it is desired to dehydrogenate the naphthenic hydrocarbons to produce aromatics, to cyclize the straight chain paraffinic hydrocarbons to form aromatics, to isomerize the normal and slightly branched chain paraffins to yield highly branched chain paraffins and to effect a controlled type of cracking which is selective both in quality and quantity.

Normal and slightly branched chain paraffinic hydrocarbons of the type contained in the above fractions have relatively low octane ratings. Highly branched-chain paraffinic hydrocarbons, on the other hand, are characterized by high octane ratings. Accordingly, one objective of reforming is to effect isomerization of the normal and slightly branched-chain paraffins to more highly branched-chain paraffins. Since aromatic hydrocarbons have much higher octane ratings than naphthenic hydrocarbons, it is also an objective of reforming to simultaneously produce aromatics in good yield. The production of aromatic hydrocarbons during reforming is effected by dehydrogenation of the naphthenic hydrocarbons and dehydrocyclization of the paraffinic hydrocarbons. Aromatic hydrocarbons are also produced by isomerization of alkyl cyclopentanes to cyclohexanes which thereafter undergo dehydrogenation to form the desired aromatics.

The above objectives of reforming are, however, generally not entirely realized since it is a characteristic of such process to isomerize paraffins mainly to mono-alkyl-paraffins, particularly in the low molecular weight range of five to seven carbon atoms. Thus, a typical reformate C₆- boiling range fraction has the following composition:

	Weight per cent
N-Hexane	27.1
2-methyl pentane	26.7
3-methyl pentane	18.9
2,2 di-methyl butane	3.7
2,3 di-methyl butane	5.2
Cyclic compounds	12.3

The remaining amount of normal paraffins represents, furthermore, the inevitable consequence of approach to thermodynamic equilibrium between normal and iso-paraffins. Thus, the material in this boiling range, by virtue of its limited content in multiple branching and the remaining high concentration of normal paraffin has a relatively low octane rating. The above fraction, for example had an octane number (Research+3 cc. TEL) of 87.8 as compared to an octane number (Research+3

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cc. TEL) of 98 for the total reformate liquid from which it was separated.

It has been a desirable objective of present technology to upgrade the quality of these light naphtha fractions. Because of the highly depressing blending octane value of such normal paraffins as n-hexane, it has heretofore been suggested to separate the same from the reformate product and either to discard them or to reprocess them in a separate isomerization system or by recycling through the reforming process with the aid of very careful fractionation between normal and iso-components, for such further processing of the fractions rich in normal components. Such fractionation has to be precise and is costly. The benefits from such previously proposed operations have, accordingly, not been well defined.

It is a major object of the present invention to provide an improved method for upgrading the product obtained upon reforming hydrocarbon mixtures to increase the octane number thereof. A further object is to improve the quality of a selected fraction of such reformate. A still further object is the provision of a method for enhancing the quality of a reformate fraction consisting essentially of hydrocarbons characterized by five to seven carbon atoms.

The above and other objects which will be apparent to those skilled in the art are achieved by the process described herein. Broadly, the present invention comprises reforming a hydrocarbon mixture, subjecting the resulting reformate to contact under catalytic cracking conditions with a catalyst of a crystalline zeolite having rigid three-dimensional networks bearing catalytic surfaces active in hydrocarbon cracking and having uniform interstitial dimensions sufficiently large to sorb normal paraffin components contained in the reformate but sufficiently small to exclude hydrocarbon components of larger molecular size. The result of such treatment is the preferential removal, by cracking, of the normal paraffin component to the exclusion of the other larger size hydrocarbon components, such as iso-paraffins and cyclic hydrocarbons. A valuable feature of this operation is the production from cracked normal paraffins of large amounts of olefins.

The use of the above crystalline zeolite cracking catalyst in this process, in contrast to the use of conventional cracking catalysts such as acid activated clays and synthetic composites of silica and alumina, gives rise to a much higher yield of olefinic products. Such products are capable of further utilization and may, in fact, be usefully combined with the isobutane product of the reforming reaction to form valuable alkylate gasoline.

Accordingly, in one embodiment, the process described herein comprises reforming a mixture of petroleum hydrocarbons, yielding a reformate containing a complex mixture of hydrocarbons including normal paraffins and components of larger molecular size, subjecting the reformate to contact under catalytic cracking conditions with a crystalline zeolite catalyst having a critical crystal port size which allows passage of only normal paraffin hydrocarbons to the exclusion of components of larger molecular size whereby the normal paraffin components are selectively catalytically cracked to yield a highly olefinic gas and a liquid product characterized by an octane number higher than the said reformate.

In another embodiment, the present invention provides a process which comprises reforming a mixture of petroleum hydrocarbons, yielding a reformate containing normal paraffins, iso-paraffins and cyclic hydrocarbon components, subjecting the reformate to contact under catalytic cracking conditions with a crystalline zeolite catalyst having a pore structure which permits passage of normal but not of iso-paraffins or cyclic hydrocarbons whereby the normal paraffin components are selectively

catalytically cracked to yield highly olefinic light gases and a liquid product and reblending said liquid product with the reformat or a selected fraction thereof.

In still another embodiment, the present process involves reforming a mixture of hydrocarbons to obtain a reformat containing normal paraffins in admixture with hydrocarbon components of larger molecular size, separating from said reformat a fraction of hydrocarbons, boiling in the C_5 to C_7 range, cracking said reformat fraction in the presence of a crystalline zeolite catalyst having a pore structure which permits passage of normal paraffins but not of larger size components whereby the normal C_5 to C_7 paraffin components are selectively catalytically cracked to highly olefinic light gases and a C_5 to C_7 liquid product and reblending said liquid product with the remaining reformat to yield a product characterized by an octane number higher than the said reformat.

In a further embodiment, the present process comprises reforming a mixture of hydrocarbons to obtain a reformat containing normal paraffins in admixture with hydrocarbon components of larger molecular size, separating from said reformat an isobutane fraction and a separate fraction of hydrocarbons, boiling in the C_5 to C_7 range, cracking said C_5 to C_7 reformat fraction in the presence of a crystalline zeolite catalyst having a pore structure which permits passage of normal paraffins but not of larger size components whereby the normal C_5 to C_7 paraffin components are selectively catalytically cracked to highly olefinic light gases and a C_5 to C_7 liquid product, combining said olefinic light gases with the aforementioned isobutane fraction under alkylation conditions to form alkylate gasoline and blending said C_5 to C_7 liquid and said alkylate gasoline with the remaining reformat to yield a product characterized by an octane number higher than said reformat.

In a still further embodiment, the present invention affords a process which comprises reforming a mixture of petroleum hydrocarbons, yielding a reformat containing normal paraffins, iso-paraffins and cyclic hydrocarbon components, separating from said reformat a fraction of hydrocarbons boiling in the C_5 to C_7 range, cracking said reformat fraction in the presence of a crystalline zeolite catalyst having a pore structure which permits passage of normal paraffins but not of iso-paraffins or cyclic hydrocarbons, whereby the normal C_5 to C_7 paraffin components are selectively catalytically cracked to highly olefinic light gases and a C_5 to C_7 liquid product, combining said C_5 to C_7 liquid product with the remaining reformat under alkylation conditions and separating from the products of alkylation a fraction boiling in the gasoline range characterized by an octane number higher than said reformat.

The initial reforming step of the present process is carried out under the conventional conditions of reforming employed in the art. Such conditions involve the use of a temperature between about 800° F. and 1000° F. and usually a temperature between about 850° F. and 975° F. The pressure during reforming is generally within the range of about 100 to about 1000 pounds per square inch gauge and more usually between about 200 and about 700 pounds per square inch gauge. The liquid hourly space velocity employed, i.e. the liquid volume of hydrocarbon per hour per volume of catalyst is between about 0.1 and about 10 and usually between 0.5 and about 4. In general, the molar ratio of hydrogen to hydrocarbon charge employed is between about 1 and about 20 and preferably between about 4 and about 12. The catalysts employed in the reforming step may be any of those conventionally used, including, for example, the oxides of group VI metals such as molybdenum, or chromium, a metal of the platinum series such as platinum, palladium, osmium, iridium, ruthenium, or rhodium deposited on a suitable support such as silica, alumina, or

components thereof. Such catalysts may have contained herein, various amounts of halogens, boron or other components designed to enhance the catalytic characteristics thereof. The hydrocarbon charge stocks undergoing reforming comprise mixtures of hydrocarbons and particularly petroleum distillates boiling within the approximate range of 60° F. to 450° F., which range includes naphthas, gasolines and kerosene. The gasoline fraction may be a full boiling range gasoline but generally is a naphtha having an initial boiling point of between about 150° F. and about 250° F. and an end boiling point of between about 350° F. and about 425° F. As will be appreciated, the above charge stocks, catalysts, and conditions are those conventionally employed in reforming operations.

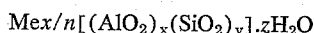
The reformat produced as a result of such operations is made up of a complex mixture of hydrocarbons including normal paraffins and components of larger molecular size, such as isoparaffins and cyclic hydrocarbons. The entire reformat, so obtained, may be subjected to subsequent catalytic cracking as described hereinbelow or a selected fraction of such reformat may be conducted to the cracking step. It is a preferred aspect of the invention to separate a light fraction from the reformat boiling in the C_5 to C_7 range and to selectively crack such separated fraction since it has been observed that it is particularly within such range that normal paraffins of low blending octane numbers are encountered. The reformat or selected fraction thereof, is, in accordance with the present invention, subjected to contact under catalytic cracking conditions with a catalyst of a crystalline zeolite having rigid three-dimensional networks bearing catalytic surfaces active in hydrocarbon cracking and having uniform interstitial dimensions sufficiently large to admit into the pores of the catalytic structure the normal paraffin components of the reformat charge, but sufficiently small to exclude hydrocarbon components of larger molecular size. The size selective cracking catalyst is essentially a solid crystalline aluminosilicate zeolite having uniform pore dimensions of about 5 Angstrom units. Under such conditions, of contact, the normal paraffin components of the charge mixture capable of entering into the interior pore structure of the above catalyst undergo cracking to highly olefinic products while the components of larger molecular size, such as iso-paraffinic and cyclic components are unable to penetrate the porous catalyst structure and accordingly undergo substantially no catalytic cracking. The selective removal, by cracking, of the normal paraffin components of the reformat charge serves to increase the overall octane number thereof since, as noted hereinabove, normal paraffins possess a low octane rating. Moreover, it has been found, following the method of the present invention, that the cracked normal paraffin components result in highly olefinic light gases and a liquid product having an octane number exceeding that of the reformat charge and that by reblending such liquid product obtained with the remaining reformat, the octane number of the latter is improved.

It is contemplated that the reaction conditions heretofore used in effecting catalytic cracking will be employed in the cracking step of the present process. Thus, catalytic cracking with the crystalline size-selective zeolite catalyst described herein may be carried out by contacting a reformat charge at catalytic cracking conditions employing a temperature within the approximate range of 700° F. to 1200° F. and preferably between about 900° F. and about 1100° F. and under a pressure ranging from sub-atmospheric pressure up to several hundred atmospheres. The liquid hourly space velocity of the charge may range from 0.2 to 4.0 and preferably from 0.5 to 2.0. The catalyst may be used as pellets in a fixed bed operation or they may be used in a compact moving bed operation or in a fluidized operation. The contact time of the reformat charge with the catalyst is adjusted in any case according to the conditions, the particular

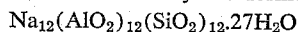
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charge stock and the particular results desired to give a substantial amount of cracking of the normal paraffin components to lower boiling highly olefinic products.

The cracking operation of the instant process is particularly characterized by the presence of a catalyst comprising a crystalline synthetic or natural zeolite having a uniform pore size which permits passage of normal paraffins but excludes larger molecular size components. It is preferred to use as cracking catalyst, a synthetic zeolite having uniform pore dimensions of about 5 Angstrom units made by dehydrating a synthetic metal aluminosilicate salt. The resulting dehydrated forms of crystalline zeolites have the atoms thereof arranged in a definite crystalline pattern. Such structure contains a large number of small cavities interconnected by a number of still smaller channels. These cavities and channels are precisely uniform in size. It is essential for the present process that the zeolite catalyst have a uniform pore structure permitting entry into the interior thereof of normal paraffin hydrocarbons but excluding entry of iso-paraffins, aromatic, naphthenes and other components characterized by a molecular size greater than that of normal paraffins. Generally, a catalyst fulfilling the above requirements has a uniform pore size of about 5 Angstrom units. Thus, if the pore size is materially smaller than 5 Angstrom units, the pores are too small to permit entry into the crystalline catalyst structure of normal paraffins. If the pores are materially larger, the large hydrocarbon molecules, i.e. iso-paraffins and cyclic compounds are able to enter the pores of the catalyst structure so that selective catalytic cracking of the normal paraffin components cannot thereby be achieved. Chemically, the zeolites employed herein as catalysts in the cracking step of the present process may be represented by the general formula:



where Me is a metal cation, x/n is the number of exchangeable metal cations of valence n , x is also the number of aluminum ions combined in the form of aluminate, y is the number of silicon atoms, and z is the number of water molecules, removal of which produces the characteristic channel system. In the above formula, y/x is a number from 1 to 5 and usually from 1 to 2. Zeolites having the above characteristics have sometimes been referred to as molecular sieves. At the present time, there are commercially available molecular sieves having channels of about 5 Angstroms in diameter. Such material known as "Molecular Sieve 5A" is essentially the crystalline calcium aluminosilicate prepared by base-exchange of a crystalline sodium aluminosilicate having channels of about 4 Angstroms in diameter, known as "Molecular Sieve 4A" and characterized by the formula:



it being understood that calcium replaces sodium in the ratio of one calcium ion for two sodium ions.

Such molecular sieves consist fundamentally of a three-dimensional structure of tetrahedral silicon and aluminum. These tetrahedra are joined by sharing oxygen atoms in such a manner that the ratio of atoms of oxygen to the total number of atoms of aluminum and silicon is equal to two. The electrovalence of the tetrahedra containing aluminum is balanced by the inclusion in the crystal of a cation, for example, an alkali metal or an alkaline earth metal cation. This equilibrium can be expressed by the formula wherein the ratio of Al_2 to the number of the various cations such as Ca, Sr, Na_2 , K_2 or Li_2 , is equal to unity. One cation may be exchanged either in entirety or partially by another cation utilizing ion exchange techniques. The spaces between the tetrahedra are occupied by molecules of water prior to dehydration.

The above molecular sieves are ordinarily prepared initially in the sodium form of the crystal. The sodium ion in such form may, as desired, be exchanged for other alkali metal or other alkaline earth metal cations. In

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general, the process of preparation involves heating, in aqueous solution, an appropriate mixture of oxides, or of materials whose chemical composition can be completely represented as a mixture of oxides Na_2O , Al_2O_3 , SiO_2 and H_2O at a temperature of approximately 100°C . for periods of 15 minutes to 90 hours or more. The product which crystallizes within this hot mixture is separated therefrom and water washed until the water in equilibrium with the zeolite has a pH within the range of 9 to 12. The material is thereafter activated by heating until dehydration is attained.

It is to be noted that the sodium form of the above zeolite, i.e. "Molecular Sieve 4A" is catalytically inactive for use as a cracking catalyst in the process of the present invention. However, such inactive form may be rendered highly active in catalytically selectively cracking normal paraffinic hydrocarbons in the present process by the simple procedure of cation exchange of calcium for sodium after crystallization. By base-exchanging the sodium aluminosilicate salt with a calcium ion-containing solution, the salt becomes catalytically active in selectively cracking normal paraffinic hydrocarbons and has a resulting uniform pore diameter of about 5 Angstrom units.

While calcium aluminosilicate characterized by uniform pores of approximately 5 Angstroms in diameter is preferred for use as the catalyst in the cracking step of the present process, it is contemplated that other metal aluminosilicates having a uniform pore size of about 5 Angstrom units may also suitably be employed as the cracking catalyst. Thus, aluminosilicate salts containing a divalent alkaline earth metal such as strontium or magnesium or other divalent metal ion, which salts are capable of sorbing at least 10 percent of their weight of n -hexane but negligible amounts of iso-hexanes when brought into contact with liquid hexanes at substantially atmospheric pressure and a temperature of about 25°C . are suitable for use in the cracking step of the present process. The sodium form of the above zeolite exchanged with calcium or other of the above-indicated divalent metals possesses larger pores than the unexchanged material. An unusual characteristic of the calcium or other divalent metal exchanged zeolite is that the opening of the pores is not accomplished progressively as the sodium ions are replaced by calcium or other divalent ions but is produced within a fairly narrow range of composition. When the exchange is 25 percent or less, the substance possesses substantially the same pore characteristics as the sodium form of the zeolite, namely a pore diameter of about 4 Angstrom units. However, when the exchange exceeds about 25 percent, the pore characteristics become those of the calcium form of the zeolite, i.e. a pore diameter of about 5 Angstrom units. Accordingly, it will be appreciated that the crystalline aluminosilicate zeolite employed as cracking catalyst in the process of the present invention may be a mixed salt of sodium and calcium or of sodium and one or more of the other above-indicated suitable divalent metal ions, it being essential that the pore diameter of the resulting composition be sufficiently large to admit normal paraffin hydrocarbons and sufficiently small to exclude hydrocarbons having a molecular size exceeding that of the normal paraffins.

It is also contemplated that the size-selective catalyst may be a composite comprising a major proportion of the above-described crystalline zeolite and a minor proportion of one or more materials which may act as promoters or activators or otherwise enhance the desired catalytic conversion while the crystalline zeolite is responsible for the major size-selective characteristics. In this regard, the crystalline zeolite may suitably be composited with activated clays, vanadia, thorina, zirconia, molybdena, silica, alumina or combinations thereof.

It is desirable, in some instances, to separate from the reformat charge a fraction boiling in the C_5 to C_7 range

and to crack such fraction in the presence of the above-described catalyst to yield highly olefinic light gases and a C₅ to C₇ liquid product and to reblend such liquid product with the remaining reformat or a selected fraction thereof. It is further often desirable to remove from the reformat charge an isobutane fraction and a separate C₅ to C₇ fraction, to crack the latter in the presence of the size-selective catalyst described herein, to yield highly olefinic light gases and a C₅ to C₇ liquid product, to combine the olefinic light gases and isobutane fraction under alkylation conditions, i.e. conditions conventionally employed in effecting alkylation of hydrocarbons including conventional alkylation catalysts, to form alkylate gasoline and to blend the aforementioned C₅ to C₇ liquid product and such alkylate gasoline with the remaining reformat. It is also desirable, in some instances, to combine the C₅ to C₇ liquid product obtained upon cracking with the remaining reformat under alkylation conditions and to separate from the products of alkylation, a fraction boiling in the gasoline range.

The various above refinements of the present invention are shown in the attached drawing wherein:

FIGURE 1 illustrates in schematic form a suitable method for upgrading a hydrocarbon charge;

FIGURE 2 illustrates in schematic form an alternate method for increasing the octane number of a hydrocarbon charge;

FIGURE 3 depicts in schematic form still another method for improving the octane number quality of a hydrocarbon charge.

Referring more particularly to FIGURE 1, a hydrocarbon mixture is conducted through line 10 to reforming zone 11 containing a suitable reforming catalyst maintained under reforming conditions. The resulting reformat is conducted through line 12 to fractionating column 13. A fraction boiling in the C₅ to C₇ range is removed from the reformat charge and conducted through line 14 to cracking zone 15 containing the above-described crystalline size-selective zeolite catalyst maintained under catalytic cracking conditions. Selective cracking of normal paraffin components contained in the C₅ to C₇ charge fraction to highly olefinic gases and a liquid rich in iso-aliphatics takes place in the cracking zone. The products resulting from cracking are removed and conducted through line 16 to fractionator 17 wherein the light olefinic gases in the C₁ to C₄ range pass overhead through outlet 18. A C₅ to C₇ liquid product is removed as bottoms from fractionator 17 and is conducted through lines 19 and 20 and reblended with the remaining reformat passing from the bottom of fractionating column 13 through line 21. The resulting product is characterized by an appreciably higher octane rating than the initially obtained reformat.

Referring now to FIGURE 2, hydrocarbon feed is conducted through line 30 to reforming zone 31 containing a suitable reforming catalyst maintained under reforming conditions. The resulting reformat is conducted through line 32 to fractionating column 33. A fraction boiling in the C₅ to C₇ range is removed from the reformat charge and conducted through line 34 to cracking zone 35 containing the herein described crystalline size-selective zeolite catalyst maintained under catalytic cracking conditions. Selective cracking of normal paraffin components contained in the C₅ to C₇ charge fraction to light highly olefinic gases and a C₅ to C₇ liquid product rich in iso-aliphatics takes place in the cracking zone. The resulting cracked products are conducted through line 36 to fractionator 37 wherein the light olefinic gases in the C₁ to C₄ range pass overhead through line 38 to alkylation zone 39 containing a suitable alkylation catalyst maintained under alkylating conditions. An isobutane fraction is removed from the reformat charge and conducted through lines 40 and 41 to alkylation zone 39. Alkylate gasoline formed in the alkylation zone is removed there-

from through line 42. A C₅ to C₇ liquid product is removed as bottoms from fractionator 37 through line 43. Such C₅ to C₇ liquid is combined in line 44 with the remaining reformat passing from the bottom of fractionating column 33 through line 45 and the alkylate passing through line 42 to yield a resulting product characterized by an appreciably higher octane rating than the initial reformat.

Turning to FIGURE 3, hydrocarbon feed is conducted through line 50 to reforming zone 51 containing a suitable reforming catalyst maintained under reforming conditions. The resulting reformat is conducted through line 52 to fractionating column 53. A fraction boiling in the C₅ to C₇ range is removed from the reformat charge and conducted through line 54 to cracking zone 55 containing the crystalline size-selective zeolite catalyst described herein maintained under catalytic cracking conditions. Selective cracking of normal paraffin components contained in the C₅ to C₇ charge fraction to highly olefinic gases and a liquid rich in iso-aliphatics takes place in the cracking zone. The products resulting from cracking are removed and conducted through line 56 to line 57 wherein it is mixed with the remaining reformat passing from the bottom of fractionating column 53 through line 58. The resulting mixture is passed through alkylation zone 59. The products of alkylation are conducted through line 60 to fractionating column 61. Light gases are removed as overhead through line 62 and materials heavier than gasoline are removed as bottoms through outlet 63. Gasoline product characterized by an appreciably higher octane rating than the initially obtained reformat is removed through line 64.

The process of this invention may be carried out in any equipment suitable for catalytic operations. The process may be operated batchwise. It is preferable, however, and generally more feasible to operate continuously. Accordingly, the process is adapted to operations using a fixed bed of catalyst. Also, the process can be operated using a moving bed of catalyst wherein the hydrocarbon flow may be concurrent or countercurrent to the catalyst flow. The moving catalyst in such operations may be in the form of a compact bed or in a fluidized state.

The following examples will serve to illustrate the process of the invention without limiting the same:

A cracking operation was carried out utilizing a catalyst of Molecular Sieve 5A. The charge stock was a 120-160° F. fraction from a 98 octane number Mid-Continent reformat obtained upon subjecting a petroleum distillate boiling in the approximate range of 180 to 380° F. with a platinum-alumina reforming catalyst under reforming conditions, involving a temperature of about 910° F., a pressure of about 500 pounds per square inch gauge, a liquid hourly space velocity of 2 and a molar ratio of hydrogen to hydrocarbon of about 10 to 1. Table I below shows the analyses of the liquid products obtained in these runs, reported as grams/100 grams charged and the conditions employed:

Table I

Example.....	1	2	3	4
Catalyst.....	Charge Stock	Molecular Sieve 5A	Molecular Sieve 5A	Vycor Chips
Temp., ° F.....		1,000	1,000	1,000
LHSV.....		1.0	0.5	0.5
G./100 g. charge:				
n-Hexane.....	27.1	18.3	15.4	28.1
2-Methyl Pentane.....	26.7	27.8	26.6	29.5
3-Methyl Pentane.....	18.9	21.5	21.3	23.9
2,2-Dimethyl Butane.....	3.7	2.4	3.5	2.9
2,3-Dimethyl Butane.....	5.2	4.2	4.5	4.6
Methyl Cyclopentane.....	5.6	4.0	3.9	4.5
Cyclohexane.....	0.1	0	0.1	0.1
Benzene.....	6.6	5.2	5.2	5.4
Research Octane No. +3 cc. TEL.....	87.8	90.7	91.6	88.5
Total Hexane Conv. Wt. Percent.....		9.1	12.6	0

The selective cracking of n-hexane is evident from Examples 2 and 3 in which a catalyst of Molecular Sieve 5A was employed. There is some cracking of isohexanes and cyclic hydrocarbons, but such is also observed in the thermal run of Example 4.

The product distribution obtained on the products resulting from Examples 2 and 3 is set forth in Table II below, based on the amount of hexane converted.

Table II

Example.....	Wt. Percent on Converted Hexane	
	2	3
Hexenes.....	6.9	5.8
Pentanes.....	16.6	11.7
Pentenes.....	4.2	3.8
Butanes.....	4.5	2.7
Butenes.....	22.1	14.9
Propane.....	11.1	12.3
Propene.....	17.3	23.4
Ethane.....	9.7	13.3
Ethylene.....	2.8	6.4
Methane.....	4.8	6.7
Total Olefins in product.....	53.3	54.3
Total Paraffins in product.....	46.7	45.7

It will be seen from the above that more than half of the hexane converted resulted in production of olefins.

Conventional cracking catalysts, such as synthetic composites of silica and alumina yield lower olefin/paraffin ratios in the products of cracking as compared to the crystalline zeolite catalysts employed in the present invention. Moreover, such conventional cracking catalysts preferentially crack iso-paraffins as compared to normal paraffins as will be evident from the data of Table III below showing the results obtained for the cracking of n-hexane and of 3-methyl pentane at a temperature of 930° F. and a liquid hourly space velocity of 1 over a catalyst of Molecular Sieve 5A and over a synthetic silica-alumina composite (90 wt. percent SiO₂—10 wt. percent Al₂O₃) respectively.

Table III

Charge Stock.....	n-Hexane		3-Methyl-pentane	
	5A	Si/Al	5A	Si/Al
Catalyst.....				
Percent Converted.....	9.6	12.9	0.9	28.5

It is accordingly to be understood that the above description is merely illustrative of preferred embodiments of the invention of which many variations may be made within the scope of the following claims by those skilled in the art without departing from the spirit thereof.

I claim:

1. A continuous method for upgrading a petroleum naphtha which comprises continuously subjecting the same to reforming, continuously removing a fraction boiling in the C₅—C₇ range from the resulting reformate, continuously contacting said fraction, containing normal paraffin hydrocarbons and hydrocarbons of larger molecular size, under catalytic cracking conditions with a cracking catalyst comprising a crystalline zeolite having a uniform pore structure of sufficient size to afford entry into the catalyst structure of the normal paraffin hydrocarbon components while excluding hydrocarbon components of larger molecular size whereby said normal paraffin hydrocarbon components are selectively cracked to a highly olefinic light gaseous product and a C₅—C₇ liquid product substantially free of olefins, having an increased iso to normal hydrocarbon ratio and a higher octane number than said petroleum naphtha and reblending said liquid product with the remaining reformate to yield a product characterized by a higher octane number than the initially formed reformate.

2. A continuous method for treating a petroleum

hydrocarbon mixture which comprises continuously subjecting the same to reforming, continuously contacting the resulting reformate containing normal paraffin hydrocarbons and hydrocarbons of larger molecular size under catalytic cracking conditions with a cracking catalyst comprising a crystalline zeolite having a uniform pore structure of sufficient size to afford entry into the catalyst structure of the normal paraffin hydrocarbon components while excluding hydrocarbon components of larger molecular size, whereby said normal paraffin hydrocarbon components are selectively cracked to a highly olefinic light gaseous product and a liquid product substantially free of olefins, having an increased iso to normal hydrocarbon ratio and a higher octane number than said hydrocarbon mixture and reblending said liquid product with a hydrocarbon material selected from the remaining reformate and fractions thereof to yield a product characterized by a higher octane number than the initially formed reformate.

3. A continuous method for treating a petroleum hydrocarbon mixture which comprises continuously subjecting the same to reforming, continuously contacting a hydrocarbon product containing normal paraffin hydrocarbons and hydrocarbons of larger molecular size selected from the group consisting of the resulting reformate and fractions thereof under catalytic cracking conditions at a temperature between about 900° F. and about 1100° F. with a cracking catalyst comprising a crystalline zeolite having a uniform pore structure of sufficient size to afford entry into the catalyst structure of the normal paraffin hydrocarbon components while excluding hydrocarbon components of larger molecular size, whereby said normal paraffin hydrocarbon components are selectively cracked to a highly olefinic light gaseous product and a liquid product substantially free of olefins, having an increased iso to normal hydrocarbon ratio and a higher octane number than said hydrocarbon mixture.

4. A continuous method for upgrading a petroleum naphtha which comprises continuously subjecting the same to reforming, continuously removing a fraction boiling in the C₅—C₇ range from the resulting reformate, continuously contacting said fraction containing normal paraffin hydrocarbons and hydrocarbons of larger molecular size under catalytic cracking conditions with a cracking catalyst comprising a crystalline zeolite having a pore size of about 5 Angstrom units in diameter, whereby said normal paraffin hydrocarbon components undergo selective cracking to a highly olefinic light gaseous product and a C₅—C₇ liquid product substantially free of olefins, having an increased iso to normal hydrocarbon ratio and a higher octane number than said petroleum naphtha and reblending said liquid product with the remaining reformate to yield a product characterized by a higher octane number than the initially formed reformate.

5. A continuous method for upgrading a petroleum naphtha which comprises continuously subjecting the same to reforming, continuously removing a fraction boiling within the C₅—C₇ range from the resulting reformate, continuously contacting said fraction containing normal paraffin hydrocarbons and hydrocarbons of larger molecular size under catalytic cracking conditions with a cracking catalyst comprising a crystalline calcium aluminosilicate having a pore size of about 5 Angstrom units in diameter, whereby said normal paraffin hydrocarbon components are selectively cracked to a highly olefinic light gaseous product and a C₅—C₇ liquid product substantially free of olefins, having an increased iso to normal hydrocarbon ratio and a higher octane number than said petroleum naphtha and reblending said liquid product with the remaining reformate to yield a product characterized by a higher octane number than the initially formed reformate.

6. A continuous method for upgrading a petroleum naphtha which comprises subjecting the same to reform-

ing, continuously removing an iso-butane fraction from the resulting reformate, continuously removing a separate fraction boiling in the C_5 - C_7 range from the resulting reformate, continuously contacting said latter fraction containing normal paraffin hydrocarbons and hydrocarbons of larger molecular size under catalytic cracking conditions with a cracking catalyst comprising a crystalline zeolite having a uniform pore structure of sufficient size to afford entry into the catalyst structure of the normal paraffin hydrocarbon components while excluding hydrocarbon components of larger molecular size, whereby said normal paraffin hydrocarbon components are selectively cracked to a highly olefinic light gaseous product and a C_5 - C_7 liquid product substantially free of olefins, having an increased iso to normal hydrocarbon ratio and a higher octane number than said petroleum naphtha, continuously combining the aforesaid iso-butane fraction and said highly olefinic light gaseous product under alkylation conditions to form alkylate gasoline, continuously combining said alkylate gasoline, the aforesaid C_5 - C_7 liquid product and the remaining reformate to yield a product characterized by a higher octane number than the initially formed reformate.

7. A continuous method for treating a petroleum hydrocarbon mixture which comprises continuously subjecting the same to reforming, continuously removing a fraction boiling in the C_5 - C_7 range from the resulting reformate, continuously contacting said fraction containing normal paraffin hydrocarbons and hydrocarbons of larger molecular size under catalytic cracking conditions with a cracking catalyst comprising a crystalline zeolite having a uniform pore structure of sufficient size to afford entry into the catalyst structure of the normal paraffin hydrocarbon components while excluding hydrocarbon components of larger molecular size, whereby said normal paraffin hydrocarbon components are selectively cracked to a highly olefinic light gaseous product and a C_5 - C_7 liquid product substantially free of olefins, having an increased iso to normal hydrocarbon ratio and a higher octane number than said hydrocarbon mixture, reblending the cracked gaseous and liquid products with the remaining reformate, contacting the resulting mixture under catalytic alkylation conditions with an alkylation catalyst and removing from the products of alkylation a material boiling in the gasoline range characterized by a higher octane number than the initially formed reformate.

8. A continuous method for treating a petroleum hydrocarbon mixture which comprises continuously subjecting

the same to reforming, continuously contacting a hydrocarbon product containing normal paraffin hydrocarbons and hydrocarbons of larger molecular size selected from the group consisting of the resulting reformate and fractions thereof under catalytic cracking conditions at a temperature between about 900° F. and about 1100° F. with a cracking catalyst comprising a crystalline zeolite having a pore size of about 5 Angstroms in diameter, whereby the normal paraffin hydrocarbon components are selectively cracked to a highly olefinic light gaseous product and a liquid product substantially free of olefins, having an increased iso to normal hydrocarbon ratio and a higher octane number than said hydrocarbon mixture and reblending said liquid product with a hydrocarbon material selected from the remaining reformate and fractions thereof to yield a product characterized by a higher octane number than the initially formed reformate.

9. A continuous method for upgrading a petroleum naphtha which comprises continuously subjecting the same to reforming, continuously removing a fraction boiling within the C_5 - C_7 range from the resulting reformate, continuously contacting said fraction containing normal paraffin hydrocarbons and hydrocarbons of larger molecular size under catalytic cracking conditions at a temperature between about 900° F. and about 1100° F. with a cracking catalyst comprising a crystalline zeolite having a pore size of about 5 Angstrom units in diameter, whereby said normal paraffin hydrocarbon components are selectively cracked to a highly olefinic light gaseous product and a C_5 - C_7 liquid product substantially free of olefins, having an increased iso to normal hydrocarbon ratio and a higher octane number than said petroleum naphtha and reblending said liquid product with the remaining reformate to yield a product characterized by a higher octane number than the initially formed reformate.

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