

[54] **SPLIT FEED REFORMING AND N-PARAFFIN ELIMINATION FROM LOW BOILING REFORMATE**

3,395,094	7/1968	Weisz.....	208/62
3,432,425	3/1969	Bodkin et al. ....	208/80
3,114,696	12/1963	Weisz.....	208/66
3,625,880	12/1971	Hamner et al.....	208/111
2,937,132	5/1960	Voorhies.....	208/64

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[52] U.S. Cl..... **208/62, 208/80, 208/92, 208/93, 208/DIG. 2**

[51] Int. Cl..... **C10g 39/00**

[58] Field of Search ..... 208/62, 66, 80, 65, 208/79, 92, 93

[57] **ABSTRACT**

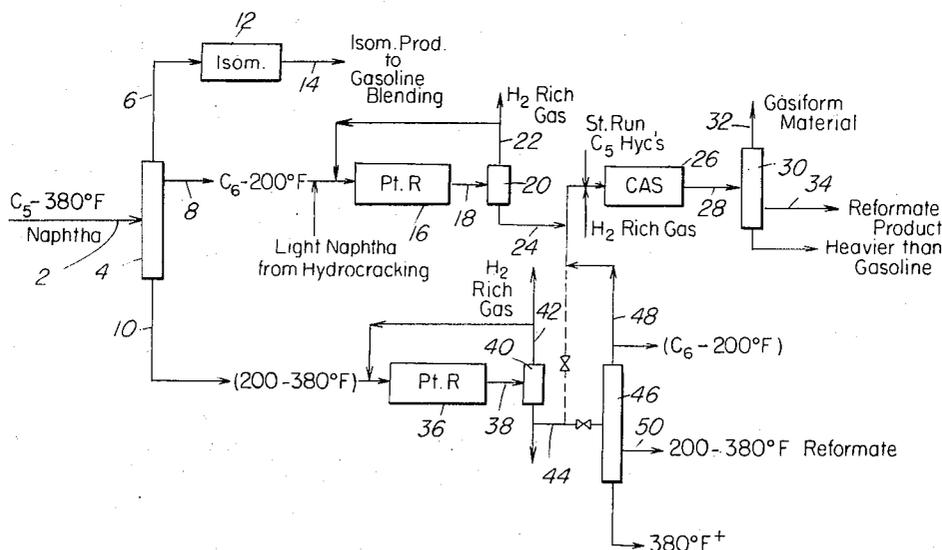
A processing combination is described for upgrading naphtha boiling range hydrocarbons by a combination of catalytic reforming and selective conversion of paraffinic components to enhance yield of aromatic hydrocarbons by contact with crystalline aluminosilicate catalysts having particular conversion characteristics.

[56] **References Cited**

**UNITED STATES PATENTS**

3,236,903 2/1966 Milton ..... 260/666

**19 Claims, 2 Drawing Figures**





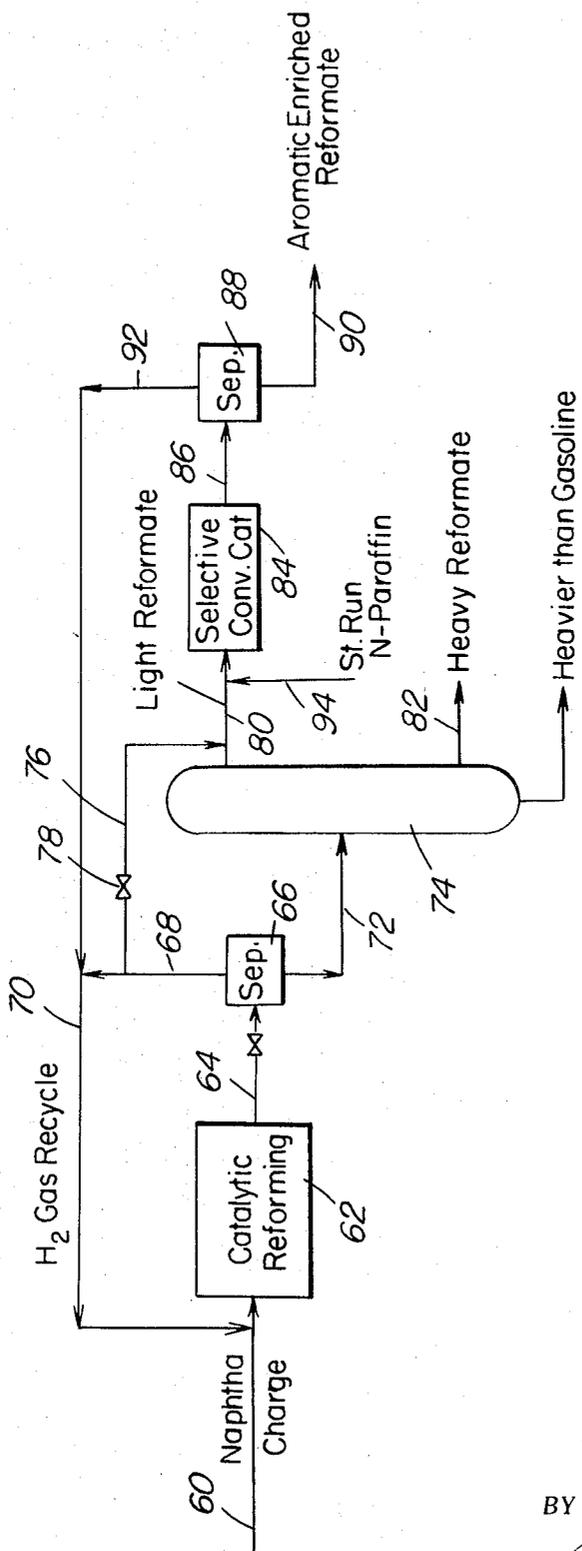


FIG. II

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## SPLIT FEED REFORMING AND N-PARAFFIN ELIMINATION FROM LOW BOILING REFORMATE

### BACKGROUND OF THE INVENTION

The art of reforming naphtha hydrocarbons boiling in the gasoline boiling range has been practiced in one form or another for many years. Over these years the reforming process has developed to include regenerative and semi-regenerative operations in combination with operations wherein the total naphtha charge is passed sequentially through a plurality of separate catalyst beds or separate fractions thereof are passed through one or more beds of reforming catalyst under condition of operating temperature, pressure and space velocity considered most suitable for achieving desired reforming reactions.

When hydrocarbons boiling in the gasoline boiling range are reformed in the presence of a hydrogenation-dehydrogenation catalyst, a number of reactions take place which include dehydrogenation of naphthenes to form aromatics, dehydrocyclization of paraffins to form aromatics, isomerization reactions and hydrocracking reactions. When the reforming conditions are quite severe, coke formation in the catalyst occurs with consequent deactivation of the catalyst. Thus, it is quite apparent that the composition of the naphtha charge will necessarily influence the severity of the reforming conditions employed to produce a desired product. However, the reforming operations, as we know them today, have certain built in limits because of reaction kinetics, catalysts available and equipment to perform the reforming operation. With the advent of unleaded gasoline requirements a renewed interest has been generated to further adapt the reforming operation for the production of high octane unleaded reformat gasoline product.

The treatment of a reformat with crystalline aluminosilicate zeolites heretofore practiced has included both physical treatments such as selective adsorption, as well as chemical treatments such as selective conversion thereof.

Although the prior art procedures for treatment of a reformat differed, nevertheless, they had one common characteristic in that substantially all involved the use of crystalline aluminosilicates having a pore size of about 5 Angstrom units. Another way of saying the same thing is to state that substantially all prior art procedures for upgrading reformates with zeolites were concerned with those zeolites which would admit normal paraffins and exclude isoparaffins. This was not too surprising since it was known in the prior art that the undesirable components in a reformat generally speaking, were normal paraffins whereas other components of a reformat, i.e., the aromatics and isoparaffins, were valuable products. Thus, the prior art directed its activities towards the use of zeolites which would selectively remove the normal paraffins and leave the aromatics and/or iso-paraffins in the reformat.

Thus, U.S. Pat. No. 2,851,970 and 2,886,508 are directed towards a reforming process where a naphtha is first reformed and the reformat or a portion thereof is contacted with a 5 Angstrom unit aluminosilicate in order to selectively sorb out the normal paraffins.

U.S. Pat. No. 3,114,696 represented a substantial improvement in the problem of upgrading a reformat

since it was directed towards the concept of treating a reformat with a crystalline aluminosilicate having a pore size of 5 Angstroms under cracking conditions so as to selectively crack out the normal paraffins.

U.S. Pat. No. 3,395,094 represented a still further advance in the overall problem of upgrading a reformat. This patent was directed towards the concept of hydrocracking the normal paraffins out of a reformat with a crystalline aluminosilicate having a pore size of about 5 Angstrom units and having hydrogenation activity limited to the internal pore structure thereof. This patent realized that not only was it necessary to selectively crack out normal paraffins, but also to preserve the aromatic constituents of the feed while this operation was being carried out.

The present invention is concerned with further improvements in the method of producing gasoline products of acceptable octane rating either with or without a lead additive (TEL) or substitutes therefor and the combination of processing steps to accomplish this purpose.

### SUMMARY OF THE INVENTION

This invention relates to the catalytic upgrading of naphtha hydrocarbons boiling over the gasoline boiling range to form higher octane gasoline product. By the present invention selected fractions of naphtha hydrocarbons are subjected to selected reforming conditions, the lower boiling fraction thereof being subjected generally to more or less severe reforming conditions than a higher boiling fraction thereof and particular reformat fractions obtained by the reforming operations are further upgraded to higher octane product by one of several different selective conversion operations for conversion of undesired low octane components.

To effect octane improvement of gasoline boiling range naphtha hydrocarbons, the present invention contemplates fractionating, for example, a straight run naphtha boiling over the entire gasoline boiling range, such as one boiling in the range of C<sub>5</sub> hydrocarbons up to about 400°F. so as to recover a C<sub>5</sub> rich fraction separately from a light naphtha fraction boiling in the range of C<sub>6</sub> hydrocarbon up to about 200°F. A heavy naphtha fraction boiling from about 200°F. up to about 400°F. is separately recovered. It is to be understood that the 200°F. cut point above recited may be varied considerably depending upon the charge naphtha composition and products desired. Therefore a cut point as low as about 158° or 180°F. may be selected or as high as 240°F. may be employed. The cut point selected may even be up as high as about 300°. In any event, the products desired from the operation of the present invention will greatly influence the cut point selected. For the purpose of this discussion a cut point of about 200°F. or 240°F. will be used since it is intended to concentrate substantially all C<sub>6</sub> hydrocarbons and a substantial portion, if not a major portion, of C<sub>7</sub> hydrocarbons into the light naphtha fraction. The light naphtha fraction thus recovered and boiling in the range of about C<sub>6</sub> hydrocarbons to about 200°F. or 240°F. is subjected to reforming operating conditions designed to convert naphthenes to aromatics and in some cases effect some isomerization of the hydrocarbon constituents employing one or more beds of suitable reforming catalyst maintained under particularly selected temperature and pressure conditions. Generally, naphthene dehydrogenation will be accomplished

in large measure in a single catalyst bed but more than one catalyst bed may be desirable and employed in the presence of an alumina containing reforming catalyst available and known in the prior art. In the event that some isomerization of n-paraffins is desired, this may be accomplished in still another bed of catalyst with a suitable reforming catalyst maintained under conditions particularly suited for this purpose.

It is generally known that a light naphtha low in naphthenes and high in paraffins is most difficult to reform. Because of this difficulty, this light naphtha material is very often left unreformed and is disposed of by blending with the product of reformed heavy naphtha.

The present invention provides a combination of catalysts operation which makes the reforming of light naphtha much more efficient and this makes it desirable to upgrade even light naphtha to a higher octane blending stock. In addition to the above, low octane n-pentane in admixture with isopentane, or in the absence thereof as the case may be, can be upgraded in octane by charging to the latter stage or light naphtha upgrading stage of the process therein defined. Thus the combination process of this invention is unique in efficiently upgrading the octane of low octane constituents. The charging of light naphtha to a platinum catalyst reforming stage and the reformat therefrom to a zeolite catalyst upgrading stage is fortuitous in that the ratio of n-paraffins and singly branched paraffins is in near optimal ratio with the quantity of aromatics necessary to give maximum product yield at a desired octane. For the same reason of optimum paraffins to aromatics ratio, a light reformat cut from a full boiling range reformat may also be charged to the zeolite upgrading stage. It is also fortuitous that a high hydrocarbon partial pressure is desirable in the zeolite upgrading stage and this is conveniently obtained by charging low boiling, low octane paraffin rich mixtures to this stage. Nevertheless it is recognized that some hydrogen partial pressure is desirable to suppress coking of the catalyst. Hydrogen is conveniently supplied by the dehydrogenation of naphthenes in the light naphtha charge over platinum reforming catalyst. If the feed is deficient in naphthenes it may be desirable to furnish supplemental hydrogen rich gas from an outside source for the purpose of maintaining a desired minimal hydrogen partial pressure.

The reformat product obtained from reforming a light naphtha fraction or otherwise obtained from a full boiling range reformat product by fractionation and having an end boiling point of about 200°F. in a specific example is thereafter subjected to a catalytic operation particularly selective for the conversion of low octane paraffins in this reformat fraction to permit ultimate recovery thereof as lower boiling paraffins (i.e., propane and butane) and as alkylated product of aromatic constituents in the reformat. Thus the removal of paraffins from naphtha boiling range material as provided in a reformat may be accomplished by contacting reformat material with a catalyst selective for converting substantially only n-paraffin components therein to the substantial exclusion of branched chain and aromatic compounds to lower boiling paraffinic components, such as is possible by contact with a small pore, 4 to 6 Angstrom crystalline zeolite cracking and/or hydrocracking catalyst. On the other hand, the reformat may be contacted with a new family of catalysts herein referred to as ZSM-5 type catalyst which have been

found to have the property of alkylating alkyl constituents existing and formed in the reformat upon contact therewith to aromatic nuclei of the reformat.

It will be recognized by those familiar with the industry that the products produced will be a function of demand and economic advantage to the producer. Thus, in some refinery operations there will be a greater demand and economic advantage for propylene and butylene rather than the saturated compound thereof and in some operations the demand for methane or LPG gases will take precedence. On the other hand, when the primary interest resides in the preparation of gasoline of acceptable unleaded octane rating, the formation of alkylated products and branched chain compounds of suitable clear octane rating of at least 94 or 95 will effect some control on the operation selected.

The high boiling naphtha fraction above identified and boiling in the range of from about 180°F. to 240°F. initially up to about 380° or 400°F. end point is subjected to a separate multiple bed reforming operation maintained under reforming conditions particularly selective to upgrade this naphtha fraction to a higher octane product of at least 90 research method octane numbers unleaded. The reforming operation selected to upgrade the high boiling portion of the naphtha charge may be of the regenerative or semi-regenerative type. Thus reforming of this heavy naphtha fraction boiling in the range of from about 180°F. and preferably from 240°F. up to about 380° or 400°F. may be accomplished at a pressure in the range of from about 50 psig up to about 400 or 500 psig in the presence of a platinum type reforming catalyst wherein the alumina support may be eta, gamma or mixed eta-gamma alumina either alone or in combination with one or more promoters including halogen such as chlorine or fluorine or a metal promoter known in the prior art. On the other hand, the reforming catalyst may be molybdenum on alumina or one of the known bimetallic reforming catalysts known in the art with or without a halogen promoter. It is also contemplated employing different catalyst compositions in the separate reforming catalyst beds which will be most effective to carry out one or more of the several catalytic reactions comprising reforming reactions.

The temperature employed during catalytic reforming will be a function of the type of operation employed as will be the space velocity. However, reforming temperatures are usually in the range of about 800°F. up to about 1000°F. or higher and the space velocity will be in the range of from about 0.1 v/v/hr up to about 3 or 5 v/v/hr. In general, the molar ratio of hydrogen to hydrocarbon charge will be from about 1 to about 20 and preferably will be from about 4 to about 8 or 10.

The catalyst employed to reform the lower boiling fraction may also be of the platinum type described above and used alone or in combination with metal promoters or a bimetallic reforming catalyst dispersed in a support material comprising primarily alumina of the eta, gamma or a mixed eta-gamma alumina type of support may be employed. The reforming catalysts may be promoted with known metal promoters used alone or in combination with a halogen promoter. On the other hand, the reforming catalyst may use halogen alone as promoter of the platinum type or bimetallic reforming catalyst and such halogen promoted catalyst may be used in only the reactors downstream of the

first reactor. Molybdenum-alumina reforming catalysts may also be employed in this operation.

The reformer effluent or reformat product obtained from the above discussed reforming operations may be separated to recover hydrogen rich gasiform material from the reformat product or hydrogen rich gasiform material may be recovered with a portion of the reformat product boiling below about 260°F. but more usually boiling below 240°F. Hydrogen rich gasiform material separated from the hydrocarbon products of the process may require separation of normally gaseous hydrocarbons from a hydrogen rich gaseous stream before recycle to the reforming operation or the selective conversion steps herein defined.

It has been found that reformat product material obtained as herein discussed and boiling in the range of from about C<sub>6</sub> hydrocarbons up to about 220°F. or 240°F. may be provided with a further octane boost and perhaps a yield boost by a selective conversion of low octane paraffin components found therein. Thus, in one embodiment a C<sub>6</sub> to 240°F. fraction obtained, as above described, may be subjected to one of the types of selective catalytic treatment described above or this fraction may be combined with a light naphtha product of hydrocracking and/or a C<sub>5</sub> normal paraffin rich fraction and thereafter subject to further conversion treatment as herein defined. On the other hand, only the C<sub>5</sub> paraffins may be added to the light reformat before contact with the conversion catalyst herein defined. In any event, it is important that the selective catalytic treatment be suitable for restructuring low octane paraffin constituents found therein as by paraffin isomerization and by paraffin cracking which results in LPG production and alkylation of low boiling aromatics with fragments of the paraffin cracking reaction.

In yet another embodiment it is contemplated passing the total naphtha charge boiling up to about 380°F. or 400°F. through a platinum catalyst reforming operation and passing a reformat product thereof boiling up to about 240°F. either before or after removal of hydrogen rich gaseous material therefrom in contact with one of the shape selective conversion catalysts herein identified to effect the desired conversion of n-paraffins and upgrading of the reformat material. On the other hand, the total reformat product of the reforming process may be passed over the selective conversion catalyst for upgrading as herein defined, care being taken to control the hydrogen partial pressure within desired limits as well as the hydrocarbon to hydrogen ratio.

In the processing combination of the present invention, it is contemplated employing a charge naphtha comprising C<sub>5</sub> hydrocarbons, which C<sub>5</sub> hydrocarbons will be initially separated from C<sub>6</sub> and higher boiling material by fractionation. It is also contemplated that some C<sub>5</sub> hydrocarbons will be formed in the separate reforming operations discussed. Therefore the processing combination of this invention will contain means in some arrangements for separating and recovering C<sub>5</sub> hydrocarbons from higher boiling hydrocarbons and these separated hydrocarbons will be subjected to further treatment as by isomerization or selective zeolite catalysis, as herein discussed.

For example, in the processing combination of this invention it is contemplated separating the effluent obtained by reforming a naphtha charge boiling from about C<sub>6</sub> hydrocarbons up to about 380°F. at about its

240° or 260°F. cut point to obtain a heavy reformat product fraction separately from reformer effluent material boiling below about 240° or 260°F. and containing hydrogen which material is thereafter processed over the selective conversion catalysts herein-defined to obtain a desired selective conversion of n-paraffins and improved octane rating of the low boiling reformat material. Hydrogen may be separated from the product of the selective conversion step for recycle to the reforming operation or the selective conversion operation.

The separate reformat product streams obtained as hereinbefore discussed and liquid products of the selective catalysis conversion can be made to serve a multipurpose use as by blending. However, since the primary purpose of the present invention is to prepare gasoline boiling range materials having an acceptable octane rating which is free or substantially free of lead additive, blending of the various octane products produced by the process will be particularly practiced to produce a relatively low octane and a high octane gasoline product free of lead. Particular blending techniques and compositions will generally be within the discretion of the refiner to produce a desired product slate and may be varied considerably within relatively wide limits depending upon the product composition and/or slate desired. It is contemplated employing the processing combination of the present invention to produce a product having a clear unleaded octane rating in the range of 90 to about 96 or 98 as well as a high octane gasoline product having an octane rating up to about 104 or 106 clear octane rating.

It is further contemplated that the upgrading reformat reactions utilized to effect catalytic cracking of n-paraffins under selective conditions with a crystalline zeolite or crystalline aluminosilicate catalyst will be carried out by contacting selected reformat product fractions with the catalyst employing temperatures in the range of 700°F. up to about 1000° or 1100°F. under essentially atmospheric or relatively high pressure conditions up to about 1000 psig. Generally, pressures below about 500 or 350 psig will be employed in the reforming step in combination with liquid hourly space velocities in the range of from about 0.1 up to about 10. Liquid hourly space velocities in the range of from about 0.5 up to about 3.0 will be used for nickel erionite shape selective conversion catalyst but above about 3 LHSV for the ZSM-5 type of conversion catalyst. The selective cracking catalyst may be employed in fixed bed, moving bed or fluid bed operations which ever offers the greatest advantage. Generally, two parallel arranged fixed catalyst beds which will permit one catalyst bed to be regenerated as required during on-stream hydrocarbon conversion in the other bed of catalyst will be an acceptable arrangement.

As mentioned above, the reformat materials may be subjected in one embodiment to a selective hydrocracking operation to form saturated products suitable as LPG products. In this selective hydrocracking operation the crystalline aluminosilicate cracking component generally has a pore size less than about 6 Angstroms and is associated with a hydrogenation component in such a manner that cracked paraffins free of olefins will be formed under selected operating conditions most suitable for that purpose. Thus the hydrogenation component may be located substantially internally, externally, or both internally and externally to

the zeolite pore structure of an erionite type of crystalline aluminosilicate and having a pore size in the range of from 4-6 Angstroms.

The characteristics of crystalline aluminosilicates having a pore size in the range of 4-6 Angstroms and their method of preparation has been the subject of several patents known in the prior art. In addition, the preparation of zeolite cracking catalyst associated with a hydrogenation component and suitable for the purpose of this invention has also been the subject of prior patent disclosure. Patents which may be referred to for the above purpose include U.S. Pat. Nos. 3,114,696 and 3,395,094.

On the other hand, the ZSM-5 type of conversion catalyst herein discussed is a crystalline aluminosilicate zeolite generally free of a hydrogenation component and provided with unusual catalytic properties. That is, the ZSM-5 type of catalyst operation herein discussed is particularly effective for treating reformat boiling in the range of C<sub>6</sub> hydrocarbons up to about 220° or 240°F. by virtue of the fact that it will effect cracking of the paraffin and alkylation of the product of paraffin cracking to monocyclic aromatic compounds thereby increasing the yield as well as the molecular weight of desired gasoline boiling range material.

The ZSM-5 type catalysts used in the novel process combination of this invention will allow entry into their internal pore structure normal aliphatic compounds and slightly branched aliphatic compounds, particularly monomethyl substituted compounds, yet substantially exclude all compounds containing at least a quaternary carbon atom or having a molecular dimension equal to or substantially greater than a quaternary carbon atom. Additionally, aromatic compounds having side chains similar to the normal aliphatic compounds and slightly branched aliphatic compounds above described could have said side chains enter the internal pore structure of the instant catalysts. Thus, if one were to measure the selectivity of the ZSM-5 type materials employed in the process of this invention, i.e., the ability to selectively sorb hexane from a mixture of the same with isohexane, these catalysts would have to be stated as being non-shape selective. It should be immediately apparent, however, that the term selectivity has a far greater significance than merely the ability to preferentially distinguish between normal paraffins and iso-paraffins. Selectivity on shape is theoretically possible at any shape or size although, quite obviously, such selectivity might not result in an advantageous catalyst for any and all hydrocarbon conversion processes.

While not wishing to be bound by any theory of operation, nevertheless, it appears that the crystalline zeolitic materials of the ZSM-5 type employed in the instant invention cannot be characterized alone merely by the recitation of a pore size or a range of pore sizes since it is also known to have a relatively high silica to alumina ratio generally above 30 and often in excess of 60 to 1. It appears also that the pore openings of these ZSM-5 type zeolites are not approximately circular in nature, as is more usually the case in many heretofore employed zeolites, but are more appropriately considered as approximately uniformly elliptical in nature. Thus, the pore openings of the ZSM-5 type of zeolitic materials have both a major and a minor axes, and the unusual and novel molecular sieving effects appear to be achieved by this elliptical shape. It appears further that the minor axis of the elliptical pores in the zeolites

apparently have an effective size of about 5.5 Angstrom units. The major axis appears to be somewhere between 6 and about 9 Angstrom units. The unique molecular sieving action of these materials is presumably due to the presence of these approximately elliptically shaped windows controlling access to the internal crystalline pore structure. In any event, irrespective of a particular molecular dimension or of the pore sizes of the ZSM-5 type catalyst the simple fact remains that outstanding results have been obtained when a hydrocarbon mixture of normal paraffins and aromatics such as provided in a low boiling reformat or portions of a light reformat effluent is converted over a ZSM-5 type catalyst. It is to be noted that the word "converted" is being employed rather than merely stating that the reformat is cracked over a ZSM-5 type catalyst for the very simple reason that the reaction mechanisms which are involved, although inclusive of cracking of normal paraffins, are far broader than that specific reaction. In fact, a novel contribution of the ZSM-5 type catalyst involves an entirely different chemistry than the chemistry which is identified as taking place in the heretofore practiced shape selective cracking over an erionite type of zeolite having a pore size of about 5 Angstrom units, i.e., a process such as that described in the aforementioned U.S. Pat. No. 3,395,094. While not wishing to be bound by any theory of operation, nevertheless, it appears that the novel contribution involves substantially more than the mere removal of normal paraffins by the selective cracking thereof to gaseous products. Although the cracking of normal paraffins does, indeed, occur, there is also occurring a simultaneous alkylation of the cracked components with at least a portion of the aromatic in the reformat feed thereby resulting in an improved yield and higher molecular weight alkylated aromatic products in the absence of significant amounts of produce LPG type of products.

It is contemplated, therefore, in one embodiment of this invention of adding to an aromatic rich fraction, a highly paraffinic fraction or a C<sub>5</sub>+ straight run gasoline fraction to, for example, a reformat material or selected portions thereof prior to its being converted over a ZSM-5 type catalyst. It has been found that a process of this type results in enhanced alkylation of particularly monocyclic aromatic components in the feed thereby resulting in a much more valuable product provided a proper balance is maintained between the paraffin and aromatic components coming in contact with the catalyst.

In its broadest form, it is clearly apparent that the present invention relates to the processing arrangement and combination of steps which will be effective for upgrading paraffin cyclic hydrocarbon mixtures and particularly naphtha boiling range hydrocarbons comprising reformates and/or selected portions of reformer effluents such as that boiling below about 260°F. and more usually below about 240°F. Thus upgrading of the hydrocarbon mixture to obtain improvement in at least its octane rating is accomplished by contact with a reforming catalyst and a selective conversion catalyst as typified by nickel erionite type of catalyst and the ZSM-5 type of catalyst herein discussed.

The conversion of reformat materials comprising paraffins and aromatic compounds may take place with or without the presence of hydrogen or a hydrogenation component in the selective catalyst composition. However, advantages in product obtained and catalyst

on-stream life are realized with different degrees of magnitude depending on catalyst employed when the amount of hydrogen in the charge contacting the conversion catalyst is present in carefully selected amounts. Thus it has been observed that too high a hydrogen partial pressure will undesirably influence the reaction mechanism of the ZSM-5 type catalyst to the point that the advantages attributed to this catalyst through alkylation are not realized. This has also been found to be true when there is an improper ratio between the normal paraffin and aromatics constituents in the charge and particularly the monocyclic aromatics in the charge. A maximum upgrading of the hydrocarbon charge through conversion over the nickel erionite type of catalyst does not rely upon the relationship of the paraffin-aromatic ratio but the catalyst life is considerably influenced by the hydrogen partial pressure and temperature operating conditions. Thus, when the ZSM-5 type of catalyst is employed down-stream of the reforming step, as provided in one embodiment of the present invention, it is believed that the alkylation effect or function attributed to the catalyst is due to the initial formation of a carbonium ion upon cracking of the normal paraffin constituents in the feed and the thus formed carbonium ion thereafter reacts with monocyclic aromatics to form alkylated aromatics. It has been found that in this ZSM-5 conversion system, the hydrogen partial pressure can be used to influence cyclization of paraffins as distinguished from alkylation of monocyclic aromatics. On the other hand, it has been found that an improper hydrocarbon to hydrogen ratio will reduce the formation of the carbonium ion and this effect will be further enhanced when the catalyst is provided with hydrogenation activity. Thus during reactions with the ZSM-5 type of catalyst it is particularly important to maintain proper ratio between paraffin and monocyclic aromatic components free of alkyl radicals in the charge as well as the hydrogen partial pressure subjected to the reaction mechanisms of this catalyst in order to reap the optimum conversion of the paraffins and alkylation thereof with the aromatics. Thus in the processing embodiment it is contemplated adding an excess of normal paraffins to the charge passed in contact with the ZSM-5 type of catalyst and such excess of normal paraffins will act to provide the desired balance between paraffin-aromatic constituents as well as influence a reduction in the hydrogen partial pressure in the operation. In view of the above, it is evident, therefore, that separation of hydrogen rich gasiform material from the reformat product may be accomplished before or after passing the selected reformat product fraction boiling below about 240°F. in contact with the ZSM-5 and nickel erionite type catalyst herein discussed.

In view of the above it is clear that the selectivity of the ZSM-5 type catalyst for effecting particularly alkylation of aromatics is influenced considerably by the operating conditions including temperature, pressure, space velocity in conjunction with the above discussed restrictions with respect to hydrogen partial pressure and hydrocarbon to hydrogen ratio.

Examples of zeolitic materials or crystalline zeolites which have been found operable as hereinafter defined are ZSM-5 type catalyst compositions disclosed and claimed in copending application Ser. No. 865,472 filed Oct. 10, 1969 now U.S. Pat. No. 3,702,886 as well as ZSM-8 crystalline zeolite compositions disclosed

and claimed in copending application Ser. No. 865,418 filed Oct. 10, 1969 now abandoned. The family of ZSM-5 catalyst compositions has the characteristic X-ray diffraction pattern set forth in Table 1, hereinbelow. ZSM-5 compositions can also be identified, in terms of mole ratios of oxides, as follows:



wherein M is a cation,  $n$  is the valence of said cation, W is selected from the group consisting of aluminum and gallium, Y is selected from the group consisting of silicon and germanium, and  $z$  is from 0 to 40. In a preferred synthesized form, the zeolite has a formula, in terms of mole ratios of oxides, as follows:



and M is selected from the group consisting of a mixture of alkali metal cations, especially sodium, and tetraalkylammonium cations, the alkyl groups of which preferably contain 2-5 carbon atoms.

In a preferred embodiment of ZSM-5, W is aluminum, Y is silicon and the silica/alumina mole ratio is at least 10 and ranges up to about 60.

Members of the family of ZSM-5 zeolites possess a definite distinguishing crystalline structure whose X-ray diffraction pattern shows the following significant lines:

TABLE I

Interplanar Spacing d(A)	Relative Intensity
11.1 ± 0.2	S
10.0 ± 0.2	S
7.4 ± 0.15	W
7.1 ± 0.15	W
6.3 ± 0.1	W
6.04 ± 0.1	W
5.97 ± 0.1	W
5.56 ± 0.1	W
5.01 ± 0.1	W
4.60 ±	W
4.25 ± 0.08	W
3.85 ± 0.07	VS
3.71 ± 0.05	S
3.64 ± 0.05	M
3.04 ± 0.03	W
2.99 ± 0.02	W
2.94 ± 0.02	W

These values as well as all other X-ray data were determined by standard techniques. The radiation was the K-alpha doublet of copper, and a scintillation counter spectrometer with a strip chart pen recorder was used. The peak heights,  $I$ , and the positions as a function of two times theta, where theta is the Bragg angle, were read from the spectrometer chart. From these the relative intensities,  $100 I/I$ , where  $I$  is the intensity of the strongest line or peak, and  $d(\text{obs.})$ , the interplanar spacing in A, corresponding to the recorded lines, were calculated. In Table 1 the relative intensities are given in terms of the symbols S = strong, M = medium, Ms = medium strong, MW = medium weak and VS = very strong. It should be understood that this X-ray diffraction pattern is characteristic of all the species of ZSM-5 compositions. Ion exchange of the sodium ion with cations reveals substantially the same pattern with some minor shifts in interplanar spacing and variation in relative intensity. Other minor variations can occur depending on the silicon to aluminum ratio of the particular sample, as well as if it has been subjected to thermal treatment. Various cation exchanged forms of ZSM-5 have been prepared. X-ray powder diffraction patterns

of several of these forms are set forth below. The ZSM-5 forms set forth below are all aluminosilicates.

TABLE 2

X-Ray Diffraction ZSM-5 Powder in Cation Exchanged Forms d Spacings Observed

As Made	HCl	NaCl	CaCl <sub>2</sub>	ReCl <sub>3</sub>	AgNO <sub>3</sub>
11.15	11.16	11.19	11.19	11.19	11.19
10.01	10.03	10.05	10.01	10.06	10.01
9.74	9.78	9.80	9.74	9.79	9.77
		9.01	9.02		8.99
8.06					
7.44	7.46	7.46	7.46	7.40	7.46
7.08	7.07	7.09	7.11		7.09
6.70	6.72	6.73	6.70	6.73	6.73
6.36	6.38	6.38	6.37	6.39	6.37
5.99	6.00	6.01	5.99	6.02	6.01
5.70	5.71	5.73	5.70	5.72	5.72
5.56	5.58	5.58	5.57	5.59	5.58
5.37		5.38	5.37	5.38	5.37
5.13	5.11	5.14	5.12	5.14	
4.99	5.01	5.01	5.01	5.01	5.01
		4.74			
4.61	4.62	4.62	4.61	4.63	4.62
		4.46			4.46
4.36	4.37	4.37	4.36	4.37	4.37
4.26	4.27	4.27	4.26	4.27	4.27
4.08		4.09	4.09	4.09	4.09
4.00	4.01	4.01	4.00	4.01	4.01
3.84	3.85	3.85	3.85	3.86	3.86
3.82	3.82	3.82	3.82	3.83	3.82
3.75	3.75	3.75	3.76	3.76	3.75
3.72	3.72	3.72	3.72	3.72	3.72
3.64	3.65	3.65	3.65	3.65	3.65
	3.60	3.60	3.60	3.61	3.60
3.48	3.49	3.49	3.48	3.49	3.49
3.44	3.45	3.45	3.44	3.45	3.45
3.34	3.35	3.36	3.35	3.35	3.35
3.31	3.31	3.32	3.31	3.32	3.32
3.25	3.25	3.26	3.25	3.25	3.26
3.17			3.17	3.18	
3.13	3.14	3.14	3.14	3.15	3.14
3.05	3.05	3.05	3.04	3.06	3.05
2.98	2.98	2.99	2.98	2.99	2.99
	2.95	2.95	2.94	2.95	2.95
2.85	2.87	2.87	2.87	2.87	2.87
2.80					
2.78			2.78		2.78
2.73	2.74	2.74	2.73	2.74	2.74
2.67			2.68		
2.66			2.65		
2.60	2.61	2.61	2.61	2.61	2.61
	2.59		2.59		
2.57		2.57	2.56		2.57
2.50	2.52	2.52	2.52	2.52	
2.49	2.49	2.49	2.49	2.49	2.49
			2.45		
2.41	2.42	2.42	2.42	2.42	
2.39	2.40	2.40	2.39	2.40	2.40
			2.38	2.35	2.38
	2.33		2.33	2.32	2.33
	2.30				
	2.24	2.23	2.23		
	2.20	2.21	2.20	2.30	
	2.18	2.18			
	2.17				
	2.13		2.13		
	2.11	2.11		2.11	
			2.10	2.10	
	2.08	2.08		2.08	
		2.07	2.07		2.08
		2.04			
2.01	2.01	2.01	2.01	2.01	2.01
1.99	2.00	1.99	1.99	1.99	1.99
			1.97	1.96	
1.95	1.95	1.95	1.95	1.95	1.95
			1.94	1.94	
	1.92	1.92	1.92	1.92	1.92
1.91				1.91	
				1.88	
1.87	1.87	1.87	1.87	1.87	1.87
	1.86				
1.84	1.84			1.84	1.84
1.83	1.83	1.83	1.83	1.83	1.83
1.82		1.81		1.82	
1.77	1.77	1.79	1.78		1.77
1.76	1.76	1.76	1.76	1.76	1.76
		1.75			1.75
	1.74	1.74	1.73		
1.71	1.72	1.72	1.71		1.70
1.67	1.67	1.67		1.67	1.67

1.66	1.66	1.65	1.66	1.66	1.66
		1.64	1.65		
		1.63	1.64		
		1.63	1.63	1.63	1.62
		1.61	1.61		1.61
1.58					
	1.57	1.57	1.57	1.57	1.57
		1.56	1.56	1.56	

Zeolite ZSM-5 can be suitably prepared by preparing a solution containing tetrapropyl ammonium hydroxide, sodium oxide, an oxide of aluminum or gallium, an oxide of silica and water and having a composition, in terms of mole ratios of oxides, falling within the following ranges:

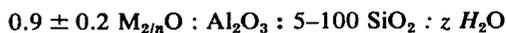
TABLE 3

	Broad	Preferred	Particularly Preferred
OH <sup>-</sup> /SiO <sub>2</sub>	0.07-1.0	0.1-0.8	0.2-0.75
R <sub>n</sub> N <sup>+</sup> /(R <sub>n</sub> N <sup>+</sup> + NA <sup>+</sup> )	0.2-0.95	0.3-0.9	0.4-0.9
H <sub>2</sub> O/OH <sup>-</sup>	10-300	10-300	10-300
YO <sub>2</sub> /W <sub>2</sub> O <sub>3</sub>	5-100	10-60	10-40

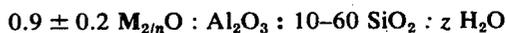
wherein R is propyl, W is aluminum and Y is silicon maintaining the mixture until crystals of the zeolite are formed. Thereafter the crystals are separated from the liquid and recovered. Typical reaction conditions consist of heating the foregoing reaction mixture to a temperature of from about 75°C to 175°C for a period of time of from about six hours to 60 days. A more preferred temperature range is from about 90 to 150°C. with the amount of time at a temperature in such range being from about 12 hours to 20 days.

The digestion of the gel particles is carried out until crystals form. The solid product is separated from the reaction medium, as by cooling the whole to room temperature, filtering, and water washing.

ZSM-5 is preferably formed as an aluminosilicate. The composition can be prepared utilizing materials which supply the appropriate oxide. Such compositions include for an aluminosilicate, sodium aluminate, alumina, sodium silicate, silica hydrosol, silica gel, silicic acid, sodium hydroxide and tetrapropylammonium hydroxide. It will be understood that each oxide component utilized in the reaction mixture for preparing a member of the ZSM-5 family can be supplied by one or more initial reactants and they can be mixed together in any order. For example, sodium oxide can be supplied by an aqueous solution of sodium hydroxide, or by an aqueous solution of sodium silicate; tetrapropylammonium cation can be supplied by the bromide salt. The reaction mixture can be prepared either batchwise or continuously. Crystal size and crystallization time of the ZSM-5 composition will vary with the nature of the reaction mixture employed. ZSM-8 can also be identified, in terms of mole ratios of oxides, as follows:



wherein M is at least one cation, n is the valence thereof and is from 0 to 40. In a preferred synthesized form, the zeolite has a formula, in terms of mole ratios of oxides, as follows:



and M is selected from the group consisting of a mixture of alkali metal cations, especially sodium, and tetraethylammonia cations.

ZSM-8 possesses a definite distinguishing crystalline structure having the following X-ray diffraction pattern:

TABLE 4

dA°	I/I <sub>o</sub>	I/I <sub>o</sub>	dA°
11.1	46	4	2.97
10.0	42	3	2.94
9.7	10	2	2.86
9.0	6	1	2.78
7.42	10	4	2.73
7.06	7	1	2.68
6.69	5	3	2.61
6.35	12	1	2.57
6.04	6	1	2.55
5.97	12	1	2.51
5.69	9	6	2.49
5.56	13	1	2.45
5.36	3	2	2.47
5.12	4	3	2.39
5.01	7	1	2.35
4.60	7	1	2.32
4.45	3	1	2.28
4.35	7	1	2.23
4.25	18	1	2.20
4.07	20	1	2.17
4.00	10	1	2.12
3.85	100	1	2.11
3.82	57	1	2.08
3.75	25	1	2.06
3.71	30	6	2.01
3.64	26	6	1.99
3.59	2	2	1.95
3.47	6	2	1.91
3.43	9	3	1.87
3.39	5	1	1.84
3.34	18	2	1.82
3.31	8		
3.24	4		
3.13	3		
3.04	10		
2.99	6		

Zeolite ZSM-8 can be suitably prepared by reacting a water solution containing either tetraethylammonium hydroxide or tetraethylammonium bromide together with the elements of sodium oxide, aluminum oxide, and an oxide of silica.

The operable relative proportions of the various ingredients have not been fully determined and it is to be immediately understood that not any and all proportions of reactants will operate to produce the desired zeolite. In fact, completely different zeolites can be prepared utilizing the same starting materials depending upon their relative concentration and reaction conditions as is set forth in U.S. Pat. No. 3,308,069. In general, however, it has been found that when tetraethylammonium hydroxide is employed, ZSM-8 can be prepared from said hydroxide, sodium oxide, aluminum oxide, silica and water by reacting said materials in such proportions that the forming solution has a composition in terms of mole ratios of oxides falling within the following range

$\text{SiO}_2/\text{Al}_2\text{O}_3$  — from about 10 to about 200

$\text{Na}_2\text{O}/\text{tetraethylammonium hydroxide}$  — from about 0.05 to 0.020

$\text{Tetraethylammonium hydroxide}/\text{SiO}_2$  — from about 0.08 to 1.0

$\text{H}_2\text{O}/\text{tetraethylammonium hydroxide}$  — from about 80 to about 200

Thereafter, the crystals are separated from the liquid and recovered. Typical reaction conditions consist of maintaining the foregoing reaction mixture at a temperature of from about 100°C to 175°C for a period of time of from about six hours to 60 days. A more preferred temperature range is from about 150° to 175°C with the amount of time at a temperature in such range being from about 12 hours to 8 days.

The ZSM-5 type zeolites used in the instant invention usually have the original cations associated therewith replaced by a wide variety of other cations according

to techniques well known in the art. Typical replacing cations would include hydrogen, ammonium and metal cations including mixtures of the same. Of the replacing cations, particular reference is given to cations of hydrogen, ammonium, rare earth, magnesium, zinc, calcium, nickel, and mixtures thereof.

Typical ion exchange techniques would be to contact the particular zeolite with a salt of the desired replacing cation or cations. Although a wide variety of salts can be employed, particular preference is given to chlorides, nitrates and sulfates.

Representative ion exchange techniques are disclosed in a wide variety of patents including U.S. Pat. Nos. 3,140,249; 3,140,251; and 3,140,253.

Following contact with the salt solution of the desired replacing cation, the zeolites may be washed with water and dried at a temperature ranging from 150°F to about 600°F and thereafter heated in air or other inert gas at temperatures ranging from about 500°F to 1500 F for periods of time ranging from 1 to 48 hours or more.

It is also possible to treat the zeolite with steam at elevated temperatures ranging from 800°F to 1600°F and preferably 1000°F and 1500°F, if such is desired. The treatment may be accomplished in atmospheres consisting partially or entirely of steam. This treatment may be accomplished within a commercial cracking unit, e.g., by gradual addition of the unsteamed catalyst to the unit.

A similar treatment can be accomplished at lower temperatures and elevated pressures, e.g., 350°-700°F at 10 to about 200 atmospheres.

A preferred embodiment of this invention resides in the use of a porous matrix together with the ZSM-5 type zeolite previously described. The ZSM-5 type zeolite can be combined, dispersed or otherwise intimately admixed with a porous matrix in such proportions that the resulting product contains from 1 percent to 95 percent by weight, and preferably from 10 to 50 percent by weight, of the zeolite in the final composite.

The term "porous matrix" includes inorganic compositions with which the aluminosilicates can be combined, dispersed or otherwise intimately admixed wherein the matrix may be active or inactive. It is to be understood that the porosity of the compositions employed as a matrix can either be inherent in the particular material or it can be introduced by mechanical or chemical means. Representative matrices which can be employed include metals and alloys thereof, sintered metals and sintered glass, asbestos, silicon carbide aggregates, pumice, firebrick, diatomaceous earths, and inorganic oxides. Inorganic compositions especially those of a siliceous nature are preferred. Of these matrices, inorganic oxides such as clay, chemically treated clay, silica, silica-alumina, etc., are particularly preferred because of their superior porosity, attrition resistance, and stability.

The compositing of the aluminosilicate with an inorganic oxide can be achieved by several methods wherein the aluminosilicates are reduced to a particle size less than 40 microns, preferably less than 10 microns, and intimately admixed with an inorganic oxide while the latter is in a hydrous state such as in the form of hydrosol, hydrogel, wet gelatinous precipitate, or in a dried state, or a mixture thereof. Thus, finely divided aluminosilicates can be mixed directly with a siliceous gel formed by hydrolyzing a basic solution of alkali metal silicate with an acid such as hydrochloric, sulfu-

ric, acetic, etc. The mixing of the three components can be accomplished in any desired manner, such as in a ball mill or other types of mills. The aluminosilicates also may be dispersed in a hydrosol obtained by reacting an alkali metal silicate with an acid or alkaline coagulant. The hydrosol is then permitted to set in mass to a hydrogel which is thereafter dried and broken into pieces of desired shape or dried by conventional spray drying techniques or dispersed through a nozzle into a bath of oil or other water-immiscible suspending medium to obtain spheroidally shaped "bead" particles of catalyst such as described in U.S. Pat. No. 2,384,946. The aluminosilicate siliceous gel thus obtained is washed free of soluble salts and thereafter dried and/or calcined as desired.

In a like manner, the aluminosilicates may be incorporated with an aluminiferous oxide. Such gels and hydrous oxides are well known in the art and may be prepared, for example, by adding ammonium hydroxide, ammonium carbonate, etc., to a salt of aluminum, such as aluminum chloride, aluminum sulfate, aluminum nitrate, etc., in an amount sufficient to form aluminum hydroxide which, upon drying, is converted to alumina. The aluminosilicate may be incorporated with the aluminiferous oxide while the latter is in the form of hydrosol, hydrogel, or wet gelatinous precipitate or hydrous oxide, or in the dried state.

The catalytically inorganic oxide matrix may also consist of a plural gel comprising a predominant amount of silica with one or more metals or oxides thereof selected from Groups IB, II, III, IV, V, VI, VII, and VIII of the Periodic Table. Particular preference is given to plural gels or silica with metal oxides of Groups IIA, III and IVa of the Periodic Table, especially wherein the metal oxide is rare earth oxide, magnesia, alumina, zirconia, titania, beryllia, thoria, or combination thereof. The preparation of plural gels is well known and generally involves either separate precipitation or coprecipitation techniques, in which a suitable salt of the metal oxide is added to an alkali metal silicate and an acid or base, as required, is added to precipitate the corresponding oxide. The silica content of the siliceous gel matrix contemplated herein is generally within the range of 55 to 100 weight percent with the metal oxide content ranging from 0 to 45 percent.

The inorganic oxide may also consist of raw clay or a clay mineral which has been treated with an acid medium to render it active. The aluminosilicate can be incorporated into the clay simply by blending the two and fashioning the mixture into desired shapes. Suitable clays include attapulgite, kaolin, sepiolite, polygarskite, kaolinite, halloysite, plastic ball clays, bentonite, montmorillonite, illite, chlorite, etc.

Other useful matrices include powders of refractory oxides, such as alumina, alpha alumina, etc., having very low internal pore volume. Preferably, these materials have substantially no inherent catalytic activity of their own.

The catalyst product can be heated in steam or in other atmospheres, e.g., air, near the temperature contemplated for conversion but may be heated to operating temperatures initially during use in the conversion process. Generally, the catalyst is dried between 150°F and 600°F and thereafter may be calcined in air, steam, nitrogen, helium, flue gas or other gases not harmful to the catalyst product at temperatures ranging from

about 500°F to 1600°F for periods of time ranging from 1 to 48 hours or more. It is to be understood that the aluminosilicate can also be calcined prior to incorporation into the inorganic oxide gel. It is also to be understood that the aluminosilicate or aluminosilicates need not be ion exchanged prior to incorporation in a matrix but can be so treated during or after incorporation into the matrix.

As has previously been stated, it is also possible to have a hydrogenation/dehydrogenation component present in the catalyst composition.

The amount of the hydrogenation/dehydrogenation component employed is not narrowly critical and can range from about 0.01 to about 30 weight percent based on the entire catalyst. A variety of hydrogenation components may be combined with either the ZSM-5 type zeolite and/or matrix in any feasible manner which affords intimate contact of the components, employing well known techniques such as base exchange, impregnation, coprecipitation, cogellation, mechanical admixture of one component with the other, and the like. The hydrogenation component can include metals, oxides, and sulfides of metals of the Periodic Table which fall in Group VIB including chromium, molybdenum, tungsten and the like; Group IIB including zinc cadmium; and Group VIII including cobalt, nickel, platinum, palladium, rhenium, rhodium and the like and combinations of metals, sulfides and oxides of metals of Group VIB and VIII, such as nickel-tungsten-sulfide, cobalt oxide-molybdenum oxide and the like.

The pre-treatment before use varies depending on the hydrogenation component present. For example, with components such as nickel-tungsten and cobalt molybdenum, the catalyst is sulfur activated. But with metals like platinum or palladium, a hydrogenation step is employed. These techniques are well known in the art and are accomplished in a conventional manner.

Within the above description of the ZSM-5 type zeolites which can be used alone or physically admixed in a porous matrix, it has been found that certain aluminosilicates provide superior results when employed in the process of this invention.

First of all, it is preferred that there be a limited amount of alkali metal cations associated with the aluminosilicates since the presence of alkali metals tends to suppress or limit catalytic properties, the activity of which as a general rule decreases with increasing content of alkali metal cations. Therefore, it is preferred that the aluminosilicates contain no more than 0.25 equivalents per gram atom of aluminum and more preferably no more than 0.15 equivalents per gram atom of aluminum of alkali metal cations.

With regard to the metal cations associated with the ZSM-5 type aluminosilicate, the general order of preference is first cations of trivalent metals, followed by cations of divalent metals, with the least preferred being cations of monovalent metals. Of the trivalent metal cations, the most preferred are rare earth metal cations, either individually or as a mixture of rare earth metal cations.

However, it is particularly preferred to have at least some protons or proton precursors associated with the aluminosilicate via exchange with ammonium compounds or acids.

Having thus provided a general discussion of the improved method of this invention reference is now made to the drawings by way of example for a more clear un-

derstanding of the processing embodiment of the method of this invention.

FIG. I identifies one arrangement of split feed reforming in combination with selective upgrading of low octane reformat product material embodying the concepts of this invention.

FIG. II identifies an arrangement of naphtha reforming in combination with a selective upgrading of the light reformat product to produce an improved low boiling reformat product material embodying the concepts of this invention.

Referring now to FIG. I of the drawings, a naphtha fraction boiling in the gasoline boiling range and comprising from about C<sub>5</sub> hydrocarbons up to about 380°F. or 400°F. is passed by conduit 2 to separator tower 4. In tower 4 the naphtha charge is separated to recover a C<sub>5</sub> rich fraction withdrawn overhead by conduit 6 from a low boiling naphtha fraction boiling in the range of C<sub>6</sub> hydrocarbons up to about 240°F. withdrawn by conduit 8 and a high boiling naphtha fraction boiling above 240°F. withdrawn by conduit 10. The C<sub>5</sub> rich fraction may be passed to isomerization upgrading in zone 12 from which an acceptable isomerization product is recovered by conduit 14. The product of isomerization may be separated by one or more different methods to isolate products suitable for blending with the reformat gasoline product. One method for effecting the separation is to pass the isomerization product in contact with a small pore (4-6 Angstroms) crystalline aluminosilicate which will be selective for separating normal from isomerized hydrocarbon material. In any event, the materials of acceptable octane rating recovered from the product of isomerization may be used for blending with and/or the production of reformat material.

The C<sub>6</sub>-200°F. naphtha fraction recovered as above described is passed by conduit 8 to reforming zone 16. Reforming zone 16 comprises one or more catalytic reactors arranged in sequence containing a reforming catalyst preferably of the platinum type wherein naphthenes are converted to aromatics as the primary reaction. With more than one reactor in sequence in the reforming operation, the operating conditions and catalyst employed may be selected to perform isomerization of the light hydrocarbons passed thereto in addition to the cyclizing reactions desired in the absence of significant hydrocracking. The reformat product obtained in zone 16 is passed by conduit 18 to a high pressure separator such as separator 20 wherein a hydrogen rich recycle gas is separated from light reformat product. Hydrogen rich recycle gas is recovered from separator 10 by conduit 22 for recycle to the reforming operation or use in other refinery operations as discussed herein. The recycle hydrogen rich gas may be treated as known in the prior art to remove undesired low boiling C<sub>1</sub> to C<sub>3</sub> or C<sub>4</sub> hydrocarbon constituents therefrom. The liquid reformat is withdrawn by conduit 24 and passed thereafter to catalytic upgrading in zone 26. Catalytic upgrading zone 26 is intended to include a plurality of operations depending on the catalyst (CAS) crystalline aluminosilicate employed to effect selective upgrading of the hydrocarbon materials passed thereto. That is, a hydrocarbon material comprising normal and isoparaffin in combination with aromatics may be upgraded as by selective cracking of paraffins to the substantial exclusion of aromatics and branched chain compounds. On the other hand, the hydro-

drocarbon material may be subjected to contact with the class of catalyst identified herein as ZSM-5 type of catalysts. It will be recognized by those skilled in the art that the catalyst selected for use in zone 26 will depend in part upon the product slate desired for a particular refinery operation. Thus, where the production of LPG gaseous product is of interest, this suggests the use of a small pore zeolite catalyst of about 5 Angstroms for the reasons discussed herein. The products of catalytic upgrading obtained in zone 26 are passed by conduit 28 to separator 30. In separator 30, normally gasiform material is separated from liquid components and withdrawn by conduit 32 for passage to other processing treatment as discussed herein. An upgraded light reformat product is withdrawn by conduit 34 for passage to gasoline storage and/or blending with material boiling above or heavier than gasoline being withdrawn from the bottom of the tower.

The heavy naphtha fraction boiling up to about 380°F. is passed to reforming zone 36. Reforming zone 36 comprises a multiple reactor reforming operation of the regenerative or semi-regenerative type known in the art wherein the heavy naphtha is passed in contact with a type of platinum reforming catalyst, such as a bimetallic reforming catalyst, and considered suitable for effecting the reforming operation herein desired at a temperature in the range of from about 700°F. up to about 1000°F or higher, employing a pressure of from about 50 psig up to several atmospheres of pressure. Generally, the reforming pressure is kept reasonably low and usually is below about 400 psig. In reforming zone 36, C<sub>7</sub> and higher boiling hydrocarbons are subjected to reaction leading to the formation of aromatic and branched chain hydrocarbons of relatively high octane rating. The reformat product of zone 36 is withdrawn by conduit 38 and passed to separator 40 wherein hydrogen rich recycle gas may be separated from liquid reformat product and withdrawn by conduit 42. A portion of the hydrogen rich recycle gas withdrawn as by conduit 22 and 42 may be separately recovered for use elsewhere in the process such as for pretreating the naphtha charge to remove sulfur, or it may be used to partially supply the hydrogen requirements of zone 26 of FIG. 1. Under some circumstances, excess hydrogen in conduit 42 may be used in reforming step 16. Thus, hydrogen produced in the reforming steps may be cascaded through the process in a manner most efficient for its utilization in the processing combination. For example, some of the withdrawn hydrogen rich gas from either zone 20 or 40 may be combined or used separately for cascade first through the reformat upgrade zone 26 from which it may be passed to the naphtha pretreater zone for effecting desulfurization of the naphtha charge. The liquid reformat product separated in 40 is withdrawn by conduit 44 and may be recovered as an acceptable reformat product or this reformat product may be further upgraded as herein described by being passed all or in part to zone 26. All of the reformat may be passed directly to zone 26 by the dotted line shown or only its lower boiling portion after being passed to separator tower 46. In separator tower 46, the liquid reformat product is separated under conditions to separate a low boiling portion of the reformat boiling in the range of from about C<sub>6</sub> hydrocarbons up to about 200°F. and as high as 260°F. but more usually not above about 240°F. from a higher boiling reformat product fraction boil-

ing up to about 380°F. from a product fraction boiling above 380°F. withdrawn from the bottom of tower 46.

The reformate product fraction boiling from about 200°F. up to about 380°F. is withdrawn from the lower portion of separator 46 by line 50 having an initial boiling point which depends in large part upon the product slate demanded of the process. The low boiling portion of the reformate separated in tower 46, on the other hand, may be used as a blending component in the preparation of regular grade gasoline. It is preferred, however, to subject this fraction to further treatment with one of the selective conversion catalysts herein described to effect the conversion of low octane normal paraffins found in the product as described above. FIG. 1 shows passing this low boiling reformate fraction obtained from separator 46 by conduit 48 to zone 26 for the desired selective catalytic treatment. It is to be understood, however, that selective treatment of this light reformate fraction may also be accomplished in a zone separate from zone 26 employing the same or a different selective catalyst composition. In any event, the light reformate product is upgraded by removing normal paraffin of low octane rating thereby improving the hydrogen purity of a gaseous stream separated from the product thereof and the product of the selective catalytic treatment of improved octane rating is then employed as a blending component to produce desired octane gasoline product.

To the extent desired the processing arrangement of FIG. I may be modified so that the zeolite treating step 26 is between reforming zone 16 and separator 20 so that the total reformate will be passed in contact with the zeolite upgrading catalyst. Furthermore, the reformate product of zone 36 may be separated after removal of hydrogen rich gases therefrom to recover a reformate material boiling below about 200°F. from higher boiling reformate material and passing the reformate boiling below 200°F. thus separated with the total reformate product from zone 16 in contact with the zeolite upgrading catalyst. In this combination, it may be desirable to add a paraffin rich stream such as pentanes to the reformate material being passed in contact with the zeolite upgrading catalyst.

FIG. II departs from FIG. I primarily in the concept that a full boiling range naphtha boiling from about C<sub>5</sub> or C<sub>6</sub> hydrocarbons up to about 380°F. is passed over a platinum reforming catalyst in a plurality of separate catalyst beds maintained under reforming conditions selected to dehydrogenate naphthenes to aromatics, cyclize and isomerize paraffins and raise the octane rating of the charge naphtha to a considerably higher level. Reforming operations to accomplish the above are well known in the prior art as indicated hereinbefore. It is known, however, that the product effluent of reforming and known as reformate in the prior art contains some low boiling component primarily n-paraffins which are of a low octane rating. Furthermore, depending upon the composition of the naphtha charge and the severity of the reforming operation, the hydrogen containing recycle gas or gasiform material will vary considerably in composition and thus hydrogen purity. Therefore the processing combination of FIG. II is intended to include an operation which will not only upgrade low boiling reformate material to a higher and more desirable octane product but considerable improvement in the purity of the hydrogen rich recycle gas may also be achieved. Therefore in the processing

combination of FIG. II, the full boiling range naphtha enters the process by conduit 60 for passage to a catalytic reforming combination or zone identified as 62. In the catalytic reforming operation anyone of the known prior art reforming catalyst may be employed, it being preferred to employ platinum type reforming catalysts and/or bimetallic reforming catalysts developed in recent years. The reforming operation may be regenerative or semi-regenerative as discussed above and usually will comprise at least three separate beds of catalyst in separate reaction zones maintained under reforming operating conditions discussed above. The reformer effluent or reformate product is thereafter normally passed to a high pressure separator first and then a low pressure separator to effect the removal of low boiling normally gasiform material from a higher boiling normally liquid reformate product. Generally hydrogen rich gaseous material is recovered from the high pressure separator for recycle to the reforming operation thereby minimizing compression costs of the process with respect to this hydrogen containing stream. In the arrangement of FIG. II, the reformer effluent is passed by conduit 64 to a separator 66 which may be a high pressure separator. In separator 66 hydrogen rich recycle gas is separated and removed by conduit 68 for recycle to the reforming step 62 by conduit 70. Liquid reformate material is withdrawn from separator 66 by conduit 72 for passage to a separator or splitter tower 74. On the other hand, bypass conduit 76 containing valve 78 is provided for passing hydrogen rich reformer effluent gases directly from the reforming separator zone 66 to conduit 80 connecting with converter 84. Splitter tower 74 is provided primarily for the purpose of separating the reformate or reformer effluent into a low boiling reformate fraction and a higher boiling reformate fraction. In this specific example the separation is made primarily for the purpose of concentrating low octane paraffin components of C<sub>8</sub> and lower boiling hydrocarbons such as C<sub>7</sub> and lower boiling constituents into a low boiling or light reformate product from a more desirable higher boiling reformate material. Thus a light reformate comprising n-paraffins and aromatics with or without added hydrogen rich gas is passed from the upper portion of splitter tower 74 by conduit 80 to converter 84 with the heavy reformate being recovered from the bottom portion of the tower by conduit 82. Under some conditions, material heavier than desired gasoline product may be recovered from the bottom of tower 74 for use as desired.

The light reformate material in conduit 80 and boiling, for example, below about 240°F. is then passed in contact with one of the selective conversion catalysts herein defined to obtain for example a desired conversion of paraffins in the light reformate and the concentration of aromatics in a product fraction subsequently recovered. For example, when employing an erionite based conversion catalyst, normal paraffins most usually will be converted to desired gaseous components such as liquid propane gas. On the other hand, when employing a ZSM-5 type of catalyst, an improvement in both hydrogen purity of gasiform material recovered therefrom and an improvement in the molecular weight and yield of aromatic constituents can be realized under particularly selected operating conditions as discussed herein. For example, when employing the ZSM-5 type of conversion catalyst in zone 84 it may be desirable to combine some straight run normal paraf-

fins such as C<sub>5</sub> paraffin with the charge stream passed thereto and introduced by conduit 94 so as to maintain, for example, the partial pressure of hydrogen within desired limits or the paraffin to aromatic ratio as herein discussed so that upgrading of this stream can be realized in conjunction with obtaining an alkylation of aromatic constituents in the light reformate feed. The product of the selective conversion operation in zone 84 is then passed by conduit 86 to separator 88. Separator 88 is provided primarily for the purpose of separating normally gaseous components such as hydrogen containing gaseous components from a higher boiling aromatic enriched product of the process. The aromatic enriched product is recovered from zone 88 by conduit 90 for passage to suitable gasoline blending pool not shown. The hydrogen rich gaseous phase is withdrawn by conduit 92 for recycle as shown.

Having thus provided a general description of the present invention and presented specific examples in support thereof, it is to be understood that no undue restrictions are to be imposed by reason thereof except as defined by the following claims.

I claim:

1. A method for upgrading a naphtha boiling hydrocarbon fraction to useful products including gasoline which comprises

separating said naphtha fraction to recover light naphtha fraction from a higher boiling naphtha fraction,

separately reforming said light and higher boiling naphtha fractions under conditions selected to produce low and higher boiling paraffin containing reformate fractions, separating hydrogen rich gaseous material separately from the low boiling paraffin containing reformate fraction boiling below 260°F and said higher boiling reformate fraction, further converting paraffins in the low boiling reformate fraction boiling below about 260°F by contact with a crystalline aluminosilicate catalyst of the ZSM-5 type selective for restructuring paraffins therein, and recovering an aromatic enriched product from said crystalline aluminosilicate catalyst contact step.

2. The method of claim 1 wherein the ratio of aromatic to paraffin in the charge to the crystalline aluminosilicate catalyst contact step is adjusted to assure an excess of paraffin.

3. The method of claim 2 wherein the paraffin is n-pentane.

4. The method of claim 1 wherein the hydrogen partial pressure of the charge to the crystalline aluminosilicate catalyst contact step is controlled to a level selected to influence the alkylation of cracked paraffin constituent with aromatics.

5. The method of claim 1 wherein the crystalline aluminosilicate catalyst contact step is effected in the substantial absence of hydrogen.

6. The method of claim 1 wherein the pressure of the crystalline aluminosilicate contact step is selected from a pressure equal to or higher than the pressure of one or both of the reforming steps.

7. The method of claim 1 wherein hydrogen rich gas in the charge to the crystalline aluminosilicate catalyst contact step is sufficient to suppress coking of the catalyst.

8. The method of claim 1 wherein a light naphtha product of hydrocracking is combined with the light naphtha fraction passed to reforming.

9. The method of claim 1 wherein the total reformate product of the high boiling naphtha fraction separated from hydrogen rich gas is passed to said crystalline aluminosilicate catalyst contact step.

10. The method of claim 9 wherein a paraffin rich fraction is combined with the light reformate material passed to said crystalline aluminosilicate contact step.

11. The method of claim 1 wherein a relationship is maintained between paraffins, aromatics and hydrogen in the light reformate fraction which will optimize the alkylation reaction in the crystalline aluminosilicate contact step.

12. The method of claim 11 wherein paraffin alkylation is enhanced by the addition of monocyclic aromatics.

13. A method for upgrading naphtha boiling range hydrocarbons to gasoline product of improved octane rating which comprises,

separating said naphtha boiling hydrocarbons into a light naphtha charge and a heavier naphtha charge, separately reforming the light and heavy naphtha charges, separating a hydrogen rich gas stream from the reformate product of each of said naphtha reforming steps, recycling separated hydrogen rich gas to the reforming step from which obtained, further separating said reformate product of said heavy naphtha reforming step into a light reformate fraction and a heavier reformate fraction, combining the thus separated light reformate fraction with the reformate product of said light naphtha charge separated from hydrogen rich gas, passing the combined light reformate material obtained as above defined in contact with a ZSM-5 type crystalline aluminosilicate catalyst having the property for restructuring paraffins by cracking, by isomerizing paraffins, by alkylating cracked paraffin constituents with aromatics present in the charge and recovering a gasoline boiling material from said crystalline aluminosilicate contact step reduced in n-paraffin components but of improved octane rating.

14. The method of claim 13 wherein hydrogen rich gases are separated from the product of said crystalline aluminosilicate catalyst contact step and recycled to the light naphtha reforming step.

15. The method of claim 13 wherein the hydrogen pressure of the crystalline aluminosilicate catalyst contact step is controlled to limit coke deposition and the ratio between paraffins and aromatics in the charge thereto is controlled to optimize aromatics production.

16. The method of claim 13 wherein paraffin restructuring of the light reformate fraction is accomplished under conditions promoting alkylation of cracked paraffins with aromatics in the presence of said crystalline aluminosilicate catalyst having said restructuring properties.

17. A method for upgrading a naphtha hydrocarbon feed fraction boiling in the range of C<sub>5</sub> hydrocarbons up to about 400°F. to useful products including gasoline which comprises

a. separating the naphtha feed fraction to recover a light naphtha boiling in the range of C<sub>6</sub> hydrocarbons through substantially C<sub>7</sub> type hydrocarbons from a higher boiling naphtha fraction,

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- b. separately reforming said light naphtha fraction and said higher boiling naphtha fraction to reformate product fractions,
- c. separately recovering hydrogen rich gases from each of said reformate product fractions for recycle to the reforming step from which it is derived,
- d. further separating the reforming product of said higher boiling naphtha fraction into a light reformate material and a heavier reformate product,
- e. combining the thus obtained light reformate material with the reformate product of said light naphtha fraction separated from hydrogen rich gases and passing the combined light reformate material in contact with a crystalline zeolite conversion catalyst of the ZSM-5 type having activity and selec-

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tivity for converting particularly paraffin components to products within the group comprising gaseous olefins, LPG gaseous products and alkyl aromatics.

18. The method of claim 17 wherein the ZSM-5 type crystalline zeolite conversion catalyst is maintained under conditions for converting substantially only normal paraffins in the reformate product to gaseous products rich in either olefins or LPG paraffins.

19. The method of claim 17 wherein the ZSM-5 type crystalline zeolite conversion catalyst is maintained under conditions to form cyclic products and alkyl aromatics.

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UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,770,614 Dated November 6, 1973

Inventor(s) RICHARD G. GRAVEN

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

- Column 1, line 30 : "known" should be --know--  
Column 7, line 21 : "face" should be --fact--  
Column 8, line 37 : "produce" should be --produced--  
Column 9, line 30 : "armoatics" should be --aromatics--  
  
Column 10, line 38 : After "+" insert --0.08--  
Column 11, line 50 : Under column "CaCl<sub>2</sub>" insert --2.17--  
Column 14, line 4 : "reference" should be --preference--  
Column 14, line 44 : "proosity" should be --porosity--  
Column 17, line 23 : "produce" should be --product--  
Column 18, line 22 : "tyep" should be --type--

Signed and sealed this 7th day of May 1974.

(SEAL)  
Attest:

EDWARD M. FLETCHER, JR.  
Attesting Officer

C. MARSHALL DANN  
Commissioner of Patents