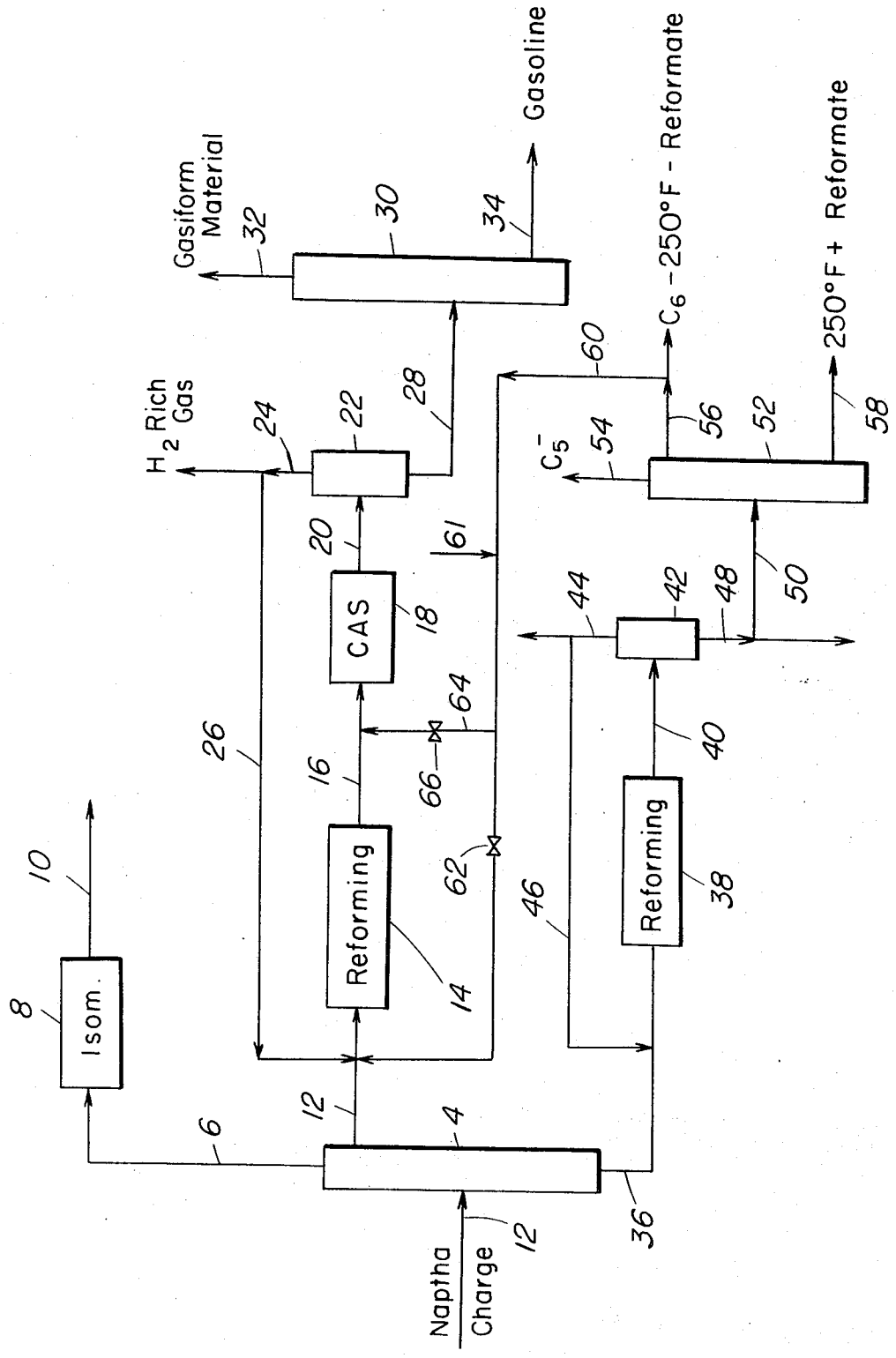
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SPLIT-STREAM REFORMING TO UPGRADE LOW-OCTANE HYDROCARBONS

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SPLIT-STREAM REFORMING TO UPGRADE LOW-OCTANE HYDROCARBONS

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ABSTRACT OF THE DISCLOSURE

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

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 conditions of operating temperature, pressure and space velocity considered most suitable for achieving desired reforming reactions.

When hydrocarbons boiling in the gasoline boiling range are formed in the presence of a dual functional hydrogenation-dehydrogenation catalyst, a number of reactions take place which include dehydrogenation of paraffins 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 of the production of high octane unleaded reformate gasoline product. Of particular importance is the upgrading of hexanes and heptanes particularly the normal and monomethyl isomers since they have very low unleaded octane numbers.

The treatment of a reformate 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 reformate 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 reformate generally speaking, were normal paraffns whereas other components of a reformate, i.e. the aromatics and iso-paraffins, 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 reformate.

Thus, U.S. Pat. Nos. 2,851,970 and 2,886,508 are directed towards a reforming process where a naphtha is first reformed and the reformate or a portion thereof is contacted with a 5 angstom unit aluminosilicate in order to selectively sorb out the normal paraffins.

U.S. Pat. 3,114,696 represented a substantial improvement in the problem of upgrading a reformate since it was directed towards the concept of treating a reformate 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. 3,395,094 represented a still further advance in the overall problem of upgrading a reformate. This patent was directed towards the concept of hydrocracking the normal paraffins out of a reformate 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 norml 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 number 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 less severe reforming conditions than a higher boiling fraction thereof and these particular reformed hydrocarbon streams obtained by the reforming operations are further upgraded to higher octane number product by selective conversion operations of conversion of less desired low octane number components.

To effect octane number 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_5 hydrocarbons up to about 400° F. so as to recover a light naphtha fraction boiling in the range of C_6 hydrocarbon up to about 200° F. from a heavy naphtha fraction boiling from about 200° F. up to about 400° F. 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 to 180° F. may be selected or 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_6 hydrocarbons and a substantial portion, if not a major portion, of C_7 hydrocarbons into the light naphtha fraction. The light naphtha fraction thus recovered and boiling in the range of about C 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 a 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 a platinum alumina type 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 platinum type 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 severely reformed heavy naphtha.

The present invention provides a combination of catalytic operations which make the reforming of light naphthas much more efficient and this makes it possible to upgrade even light naphthas to higher octane number blending stocks. In addition to the above, low octane number n-pentane in admixture with isopentane, or in the absence thereof as the case may be, can be upgraded by charging to the latter stage or light naphtha upgrading stage of the process herein defined. Thus the combination process of this invention is unique in efficiently upgrading the octane number of low octane number constituents. The charging of light naphtha to the platinum catalyst reforming stage and the reformate therefrom to the zeolite 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. It is hypothesized 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 reformate product obtained from reforming a light naphtha fraction and having an end boiling point in the range of about 200° F. to 260° F. and particularly about 250° F. in a specific example is thereafter subjected to a catalytic operation particularly selective for the conversion of n-paraffin and singly branched paraffins namely monomethyl paraffins in this reformate fraction to permit ultimate recovery thereof as lower boiling paraffins and as alkylated product of aromatic constituents in the reformate. Thus the removal of n-paraffins and monomethyl paraffins from naphtha boiling range material as provided in a reformate may be accomplished by contacting reformate material with the catalyst herein defined which is selective for converting substantially only n-paraffin and monomethyl paraffin components therein to the substantial exclusion of converting high octane multiple branched chained paraffins.

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 and up to about 360 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 360 or 400° F. may be accomplished at a pressure in the range of from about 50 p.s.i.g. up to about 400 or 500 p.s.i.g. in the presence of a suitable 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 one of the known bimetallic reforming catalyst known in the art and comprising a halogen promoter. It is 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 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.

The reformer effluent or reformate product obtained from the above discussed reforming operations may be separated to recover hydrogen rich gasiform material from the reformate product or hydrogen rich gasiform material may be recovered with a portion of the reformate 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 reformate product material obtained as herein discussed and boiling in the range of from about C_6 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 number normal and monomethyl paraffins components found therein. Thus, in one embodiment a C_6 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, for example, a light naphtha product of hydrocracking, hydrogenated products of light coker product and light TCC or FCC gasoline cuts, paraffin rich raffinate of extraction processes, and/or a C_5 normal paraffin rich fraction and thereafter subjecting the mixture to further conversion treatment as herein defined. In any event, it is important that the selective crystalline aluminosilicate catalyst have characteristics suitable for upgrading low octane number

p-paraffin and monomethyl paraffin constituents found in reformate material to alkylated aromatic components as discussed herein.

In the processing combination of the present invention, it is contemplated employing a charge naphtha comprising C_5 hydrocarbons, which C_5 hydrocarbons will be initially separated from C_6 and higher boiling material by fractionation. It is also contemplated that some C_5 hydrocarbons will be formed in the separate reforming operations discussed. Therefore the processing combination of this invention may contain means in some arrangements for separating and recovering C_5 hydrocarbons from higher boiling hydrocarbons and these separated C_5 hydrocarbons may be subjected to further treatment as by isomerization.

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_6 hydrocarbons up to about 380° F. at about its 240 or 260° F. cut point to obtain a heavy reformate 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 reformate 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 reformate product streams obtained as hereinbefore discussed and liquid products of the selective catalysis conversion can be made to serve a multi-purpose 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 products having a clear unleaded octane rating in the range of about 95 to 110.

It is further contemplated that the upgrading reactions utilized to effect catalytic cracking of normal and monomethyl paraffins under selective conditions with a crystalline zeolite or crystalline aluminsilicate catalyst will be carried out by contacting selected reformed hydrocarbon streams with the catalyst employing temperatures in the range of 550° F. up to about 900° F. and pressure from atmopsheric to relatively high pressure conditions of 1000 p.s.i.g. Generally, pressures below about 500 or 350 p.s.i.g. 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 100 will be used over the crystalline zeolite catalyst. The selective cracking catalyst may be employed in fixed bed, moving bed or fluid operations whichever offers the greatest advantage. Generally, periodic regeneration of a fixed bed or two parallel arranged fixed catalyst beds which will permit one catalyst bed to be regenerated as required during on-stream hydrocarbon conversion would be an acceptable arrangement.

The catalytic cracking of normal and monomethyl paraffins under selective conditions is carried out with a particular crystalline aluminosilicate referred to herein as a ZSM–5 type catalyst. Copending applications making reference to this type catalyst are application Ser. No. 865,472 (now U.S. Pat. 3,702,886), filed Oct. 10, 1969; application 101,231, filed Dec. 24, 1970; application 119,047, filed Feb. 25, 1971 and application 126,092 filed Mar. 19, 1971. Application 106,837 was filed concurrently with the present application on Jan. 15. 1971.

The ZSM–5 type of conversion catalyst herein discussed is a crystalline aluminosilicate zeolite with unusual catalytic properties. That is, the ZSM–5 type of catalyst operation herein discussed is particularly effective for treating reformate material boiling up to about 220 or 300° F. by virtue of the fact that it will effect cracking of low octane normal and monomethyl paraffins and effect alkylation and paraffin cyclization of the product of paraffin cracking to form 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 convert normal aliphatic compounds and slightly branched aliphatic compounds, particularly monomethyl substituted compounds, yet substantially not convert all compounds containing at least a quaternary carbon atoms or having a molecular dimension equal to or substantially greater than a quaternary carbon atom. 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-shaped 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 and monomethyl paraffins and aromatics such as provided in a low boiling reformate or portions of a light reformate 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 reformate 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 and monomethyl 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. 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 cracking of monomethyl paraffins and a simultaneous alkylation of the cracked components with at least a portion of the aromatic in the reformate feed thereby resulting in an improved yield and higher molecular weight alkylated aromatic products.

Thus it is contemplated as suggested above of adding an aromatic rich fraction, a highly paraffinic C_5 fraction or a C_5^+ straight run gasoline fraction to, for example, the product of reforming 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 types and concentration of 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 and aromatic hydrocarbon mixtures and particularly naphtha boiling range hydrocarbon products of reforming and/or selected portions of reformer effluents such as that boiling below about 300° F. and more usually below about 260° F. Thus upgrading of the naphtha boiling 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 the ZSM–5 type of catalyst herein discussed.

The conversion of reformate materials comprising normal and monomethyl 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 when hydrogen and hydrogenation component is employed.

When the ZSM–5 type of catalyst is employed downstream of the reforming step, as provided in the present invention, it is believed that the alkylation effect or function attributed to the catalyst is due to the initial formation of an olefin upon cracking of the normal paraffin constituents in the feed and the thus formed olefin thereafter reacts with monocyclic aromatics to form alkylated aromatics. With the ZSM–5 type of catalyst it is particularly important to maintain proper ratio between normal and monomethyl paraffins and monocyclic aromatic components in the charge in order to reap an optimum conversion of the paraffins and alkylation thereof with the aromatics. Some new aromatic rings will be formed by virtue of cyclization of unsaturated fragments of paraffin cracking.

In view of the above it is clear that the selectivity of the ZSM–5 type catalyst for effecting particularly alkylation of aromatic is influenced considerably by the operating conditions including temperature, hydrogen and hydrocarbon partial and space velocity.

Examples of zeolitic materials or crystalline zeolites which have been found operable as hereindefined are ZSM–5 type catalyst compositions disclosed and claimed in copending application Ser. No. 865,472 filed Oct. 10, 1969 as well as ZSM–8 crystalline zeolite compositions disclosed and claimed in copending application Ser. No. 865,418 filed Oct. 10, 1969. 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:

$$0.9\pm0.2M_{2/n}O:W_2O_3:5;100YO_2:zH_2O$$

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:

$$0.9\pm2.0M_2O:Al_2O_3:5–100SiO_2:zH_2O$$

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 1

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±0.08	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 2 times theta, where theta is the Bragg angle, were from the spectrometer chart. From these the relative intensities, $100I/I$, where I is the intensity of the strongest line or peak, and d(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	$CaCl_2$	$ReCl_3$	$AgNO_3$
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		4.46
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
				2.97	
	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	2.17		
	2.13		2.13		
	2.11	2.11		2.11	
			2.10	2.10	
	2.08	2.08		2.08	2.08
		2.07	2.07		
			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	
				1.94	
	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	
1.82		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		1.66	1.66	1.66
		1.65	1.65		
		1.64	1.64		
	1.63	1.63	1.63	1.63	1.62
	1.61	1.61	1.61		1.61
1.58					
	1.57	1.57		1.57	1.57
		1.56	1.56	1.56	

Zeolite ZSM–5 can be suitably prepared by preparing a 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^-/SiO_2	0.07–1.0	0.1–0.8	0.2–0.75
$R_4N^+/(R_4N^+ + Na^+)$	0.2–0.95	0.3–0.9	0.4–0.9
H_2O/OH^-	10–300	10–300	10–300
YO_2/W_2O_3	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:

$$0.9\pm0.2M_{2/n}O:Al_2O_3:5\text{–}100SiO_2:zH_2O$$

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:

$$0.9\pm0.2M_{2/n}O:Al_2O_3:10\text{–}60SiO_2:zH_2O$$

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

d (A.):	I/I_o	*d* (A.):	I/I_o
11.1	46	3.04	10
10.0	42	2.99	6
9.7	10	2.97	4
9.0	6	2.94	3
7.42	10	2.86	2
7.06	7	2.78	1
6.69	5	2.73	4
6.35	12	2.68	1
6.04	6	2.61	3
5.97	12	2.57	1
5.69	9	2.55	1
5.56	13	2.51	1
5.36	3	2.49	6
5.12	4	2.45	1
5.01	7	2.47	2
4.60	7	2.39	3

TABLE 4—Continued

d (A.):	I/I_o	d (A.):	I/I_o
4.45	3	2.35	1
4.35	7	2.32	1
4.25	18	2.28	1
4.07	20	2.23	1
4.00	10	2.20	1
3.85	100	2.17	1
3.82	57	2.12	1
3.75	25	2.11	1
3.71	30	2.08	1
3.64	26	2.06	1
3.59	2	2.01	6
3.47	6	1.99	6
3.43	9	1.95	2
3.39	5	1.91	2
3.34	18	1.87	3
3.31	8	1.84	1
3.24	4	1.82	2
3.13	3		

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

SiO_2/Al_2O_3—from about 10 to about 200

Na_2O/tetraethylammonium hydroxide—from about 0.05 to .020

Tetraethylammonium hydroxide/SiO_2—from about 0.08 to 1.0

H_2O/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 preference 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. Pats. 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 150°° 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.

The aluminosilicates can be mixed with inorganic oxides 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, sulfuric, 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 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 I–B, 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 II–A, III and IV*a* 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, seipiolite, 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 10 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 VI–B including chromium, molybdenum, tungsten and the like; Group II–B 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 VI–B 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 equivalent per gram atom of aluminum and more preferably no more than 0.15 equivalent per gram atom of aluminum of alkali metal cations.

With regard to the metal cations associated with the ZSM–5 aluminosilicate, the general order of preference is first cations of trivalent metals, followed by cations of divalent metals, which 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 had to the drawings by way of example for a more clear understanding of the processing embodiment of the method of this invention.

Referring now, by way of example, to the drawing, a low boiling hydrocarbon charge material such as a naphtha hydrocarbon boiling up to about 380° F. is introduced to the process by conduit **2** communicating with fractionator **4**. In fractionator **4**, a separation of the naphtha charge is made to separate C_5 hydrocarbons from a light naphtha fraction boiling from about C_6 hydrocarbons up to about 220° F. The end point of the light naphtha fraction may be selected from within the range of 170° F. up to about 250° F. A heavy naphtha fraction is withdrawn from the lower portion of fractionator **4** having an initial boiling point selected from within the range of 170 to 250° F. and an end boiling point of about 380° F. The separated C_5 hydrocarbons are withdrawn by conduit **6** and conveyed to isomerization zone **8** from which product is withdrawn by conduit **10**.

The separated light naphtha is withdrawn by conduit **12** and passing to reforming zone **14**. Reforming zone **14** may be a typical three reactor reforming system known in art for use with a platinum type reforming catalyst or some other suitable reforming catalyst. Under some circumstances this reforming system may be a two catalyst bed system which employs the same or different reforming catalysts in the separate catalyst beds. In any event the total effluent of the reforming operation is then passed by conduit **16** to zone **18** containing one or more beds of the particular crystalline aluminosilicate conversion catalyst hereinbefore defined and suitable for restructuring normal and mono branched paraffins as discussed above. The total product of the crystalline catalyst contact is then passed by conduit **20** to a separator **22**. In separator **22**, hydrogen rich gaseous material is separated from the converted naphtha product and withdrawn by conduit **24**. Conduit **26** is provided for recycling separated hydrogen rich gas to the reforming operation if desired or the separated hydrogen rich gas may go to a clean up step as desired. The remaining product is removed from the bottom of separator **22** and passed by conduit **28** to fractionator or splitter tower **30**. In zone **30** gasiform material boiling below desired hydrocarbon product is removed from the upper portion of the zone by conduit **30** with gasoline product of improved octane rating removed from the bottom of the tower by conduit **34**.

The heavy naphtha hydrocarbons in conduit **36** are passed to reforming zone **30** for upgrading by any one of several different reforming operations known in the art. The total product of the reforming operation is then passed by conduit **40** to separator **42**. In seperator **42**, hydrogen rich recycle gas is separated from the reformer effluent and removed by conduit **44**. All or part of the separated hydrogen rich gas may be recycled to reforming operation **38**. On the other hand any excess hydrogen produced in the process may be employed to supply a portion of the hydrogen required in the reforming operation **14**. Excess hydrogen in conduit **44** not recycled by conduit **46** may be furnished to other processes having a hydrogen demand. The reformer product is then withdrawn from zone **4** by conduit **48** and passed by conduit **50** to fractionator tower **52**. A portion of the reformer product may be recovered from the process as shown without passage to fractionator **52**. In fractionator **52**, the reformer effluent is separated to recover C_5 and lighter hydrocarbons withdrawn by conduit **54** from a light reformate fraction recovered by conduit **58**. As mentioned hereinbefore the separation in cut point between the light and heavy reformate product may vary considerably and be selected from within the range of 220° F. up to about 300° F. Generally and for the purpose of this discussion the cut point is about 250° F.

In the embodiments of this invention, the light reformate material in conduit **56** is subjected to a further upgrading by contact with the crystalline aluminosilicate

catalyst in zone 18 by passage through conduits 60 and 64 communicating therewith. On the other hand, it may be desirable under some circumstances to pass all or a portion of this light reformate material in conduit 60 to the inlet of reformer 14. Provisions are also made for adding additional hydrocarbon material as mentioned above such as light TCC and FCC gasoline and other materials by way of conduit 61.

Having thus provided a general discussion of the invention and described a specific processing combination, in support thereof by way of examples, it is to be understood that no undue restrictions are to be imposed by reasons thereof except as expressed in the appended claims.

We claim:

1. A method for improving the octane rating of naphtha boiling hydrocarbons which comprises

separating the naphtha into a low boiling naphtha fraction and a higher boiling naphtha fraction,

separately reforming said separated naphtha fractions to produce reformer effluents,

separating the reformer effluent of said higher boiling naphtha fraction into a hydrogen-rich gaseous phase and a reformate product, passing the reformer effluent of said low boiling naphtha fraction in contact with a crystalline aluminosilicate restructuring catalyst having an X-ray diffraction pattern as set forth in Table 1, and having the property of cracking normal and monomethyl paraffins to form constituents which alkylate with low boiling aromatics and recovering a product effluent from said crystalline aluminosilicate contact step of improved octane rating.

2. The method of claim 1 wherein the product effluent of said crystalline aluminosilicate contact step is separated to recover an aromatic rich fraction which is thereafter used to blend with the reformate product of said higher boiling naphtha fraction.

3. The method of claim 1 wherein the higher boiling naphtha reformer effluent is separated to recover low boiling reformate product having an end boiling point in the range of 240° F. to 260° F. from higher boiling reformate product and said low boiling reformate product is passed in contact with said crystalline aluminosilicate restructuring catalyst.

4. The method of claim 1 wherein a low boiling hydrocarbon stream selected from the group consisting of paraffin rich naphtha boiling range material and aromatic rich naphtha boiling range material is combined with the reformer charge material prior to contacting the crystalline aluminosilicate restructuring catalyst.

5. The method of claim 1 wherein a gasoline boiling range product of either thermal or catalytic cracking is initially hydrogenated and then combined with reformate passed in contact with the crystalline aluminosilicate restructuring catalyst.

6. The method of claim 1 wherein a portion of the hydrogen rich gases separated from the higher boiling naphtha reformer effluent is supplied to the low boiling naphtha reforming step.

7. The method of claim 1 wherein constituents formed by cracking normal and monomethyl paraffins during contact with said crystalline aluminosilicate restructuring catalyst are cyclized to form aromatics.

8. In a process for split feed reforming wherein naphtha is separated into a heavy fraction boiling above a separation temperature between about 158° F. and about 300° F. and a light fraction boiling below such separation temperature, each of said fractions is separately reformed in the presence of hydrogen under conditions to at least dehydrogenate naphthenes contained therein to aromatics with consequent generation of hydrogen, products of each of such reforming steps is separated to provide a gaseous fraction rich in hydrogen and a liquid hydrocarbon fraction of enhanced octane number as compared to the fraction so reformed and at least a part of said gaseous fraction is recycled for admixture with fresh charge to the respective reforming step; the improvement which comprises contacting the effluent of the light fraction reforming step with a crystalline aluminosilicate conversion catalyst characterized by a pore size to selectively crack normal and monomethyl paraffins without substantial conversion of paraffins containing quaternary carbon atoms, having an X-ray diffraction pattern conforming to Table 1, and passing the effluent of such selective conversion to separation of hydrogen rich gaseous fraction as aforesaid.

9. The process of claim 8 wherein said separation temperature is 200° F. to 240° F.

10. The method of claim 1 wherein said low boiling naphtha fraction boils predominantly below 200° F. and said high boiling naphtha fraction boils predominantly above 200° F.

11. The process of claim 8 wherein said separation temperature is 200° F. to 240 °F.

12. The method of claim 1 wherein said light naphtha is constituted predominanly by hydrocarbons of six and seven carbon atoms.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,753,891 Dated August 21, 1973

Inventor(s) RICHARD G. GRAVEN and HEINZ HEINEMANN

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 71 : "paraffns" should read --paraffins--

Column 5, line 1 : "p-paraffin" should read --n-paraffin--

Column 9, line 73 : After "a" insert --solution containing tetrapropyl ammonium hydroxide,--

Signed and sealed this 27th day of November 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

RENE D. TEGTMEYER
Acting Commissioner of Patents