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Bonacci et al.

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[54] **OCTANE CRACKING**

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[51] **Int. Cl.** **C10g 39/00**; C10g 35/08

[58] **Field of Search** 208/62, 65, 138, 111, 66

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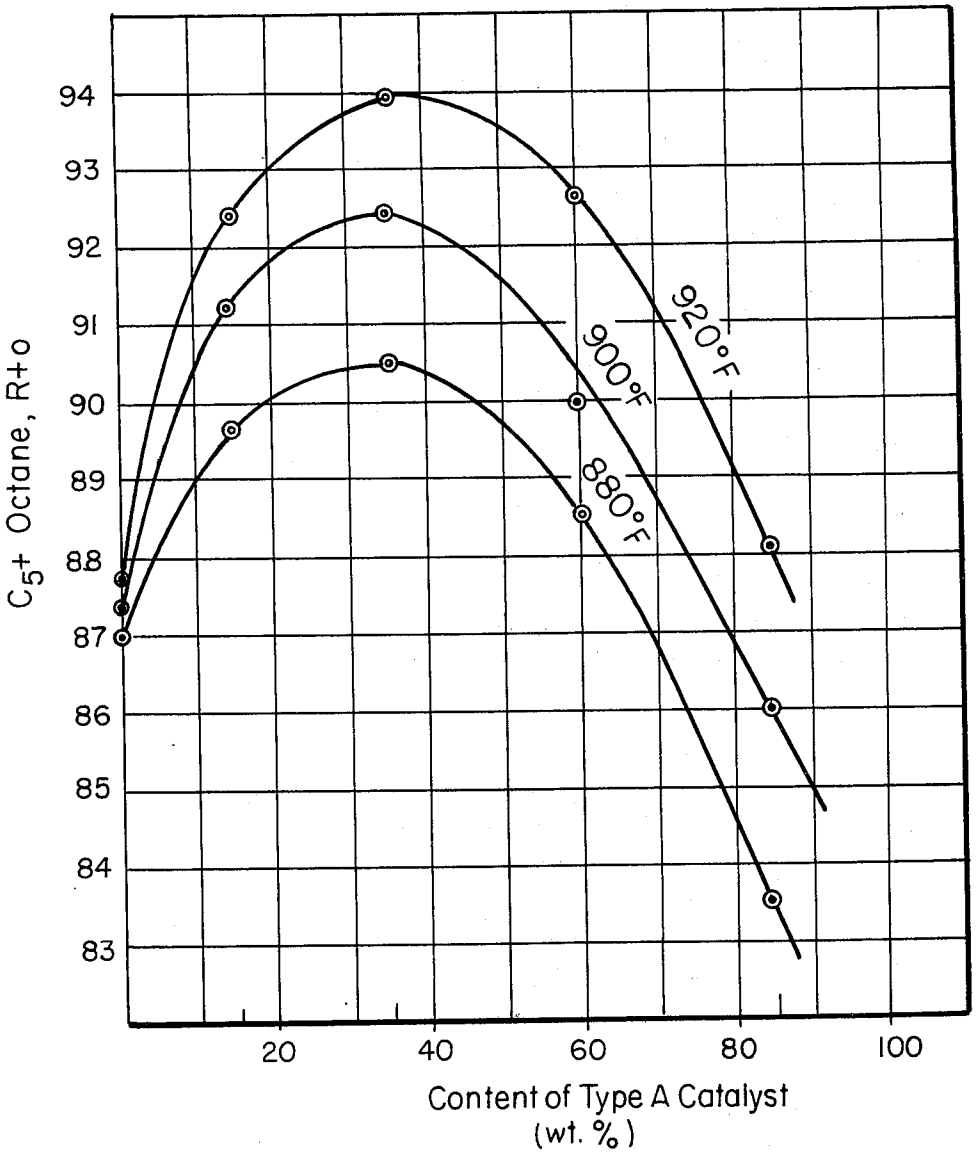
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[57] **ABSTRACT**

This disclosure relates to the method of improving the activity of shape selective hydrocracking processes by the particular combination of reforming catalyst and shape selective hydrocracking catalyst. The relationship of operating conditions is particularly concerned with the disclosure of FIG. 1 wherein it is shown that the activity for the shape selective hydrocracking process can be significantly improved through the use of an admixture of a shape selective cracking catalyst having a pore diameter of about 4.5 to 6.0 A., and reforming catalyst in a relative concentration of about 20 to 50 weight percent reforming catalyst. In a preferred embodiment, the minimum research octane increase of the naphtha or reformate across a reactor containing such a catalyst mixture is about 6 to about 10 clear octane numbers.

7 Claims, 2 Drawing Figures

FIG.1


94
93
92
91
90
89
88
87
86
85
84
83
C_5+ Octane, R+o
920°F
900°F
880°F
20
40
60
80
100
Content of Type A Catalyst
(wt. %)

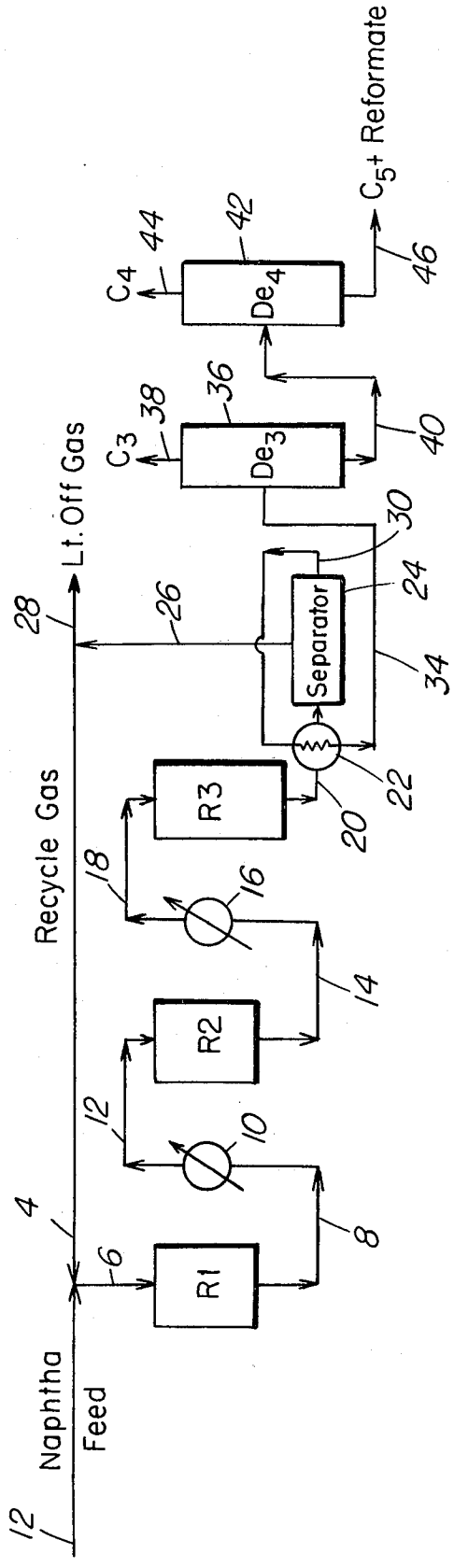

Naphtha Feed
12
Recycle Gas
4
Lt. Off Gas
28
R1
R2
R3
6
8
10
12
14
16
18
20
22
24
26
30
34
Separator
De3
De4
C3
C4
36
38
40
42
44
46
C5+ Reformate

FIG. 2

OCTANE CRACKING

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to methods and processes for converting petroleum naphthas and reformates selectively to high octane gasoline with a minimum aromatics concentration and to propane. In one aspect, the present invention is directed to one or more methods for selectively conducting chemical reactions with an arrangement of catalytic compositions possessing particular selective conversion properties with respect to different hydrocarbon components in a naphtha boiling feed or reformate thereof. More particularly, the present invention relates to effecting the selective catalytic conversion of hydrocarbon components comprising ring, normal and iso-paraffin hydrocarbon components in a hydrocarbon rich conversion process maintained under operating conditions to produce product high in octane but low in aromatics concentration and LPG (Liquid Petroleum Gas, e.g. propane) rich gaseous material.

2. Description of the Prior Art

The octane number (ON) of gasoline depends on the character and content of its various components. Presently practiced processes for obtaining high octane gasolines from naphthas are known to include reforming processes. Of these, the platinum catalytic reforming process is the one most commonly employed. During reforming the gasoline boiling range components of the naphtha boiling above about C_5 hydrocarbons are subjected to a plurality of reactions with isomerization, cyclization, aromatization and hydrogenative cracking as the major resulting transformations. While these reactions all participate in accomplishing a gain in octane number quality, such reforming operations have always been accompanied by a loss of volume or quantity of gasoline boiling range product. As is well known, progressively greater yield losses and/or shorter cycle lengths must be accepted in exchange for improvements in octane quality, as higher process severity is employed, that is, the greater the ON (octane number) quality target is.

Of particular relevance in the prior art is U.S. Pat. No. 3,395,094 which discloses the employment of a reforming catalyst and a shape selective catalyst, in cooperation with each other, in order to increase performate yield at a given target octane.

It is an object of this invention to provide an improved method and process for upgrading naphtha boiling hydrocarbons.

It is a further object of this invention to provide aromatic concentrates from naphtha boiling hydrocarbon fractions.

It is a still further object of this invention to provide an improved method and process for selectively upgrading the components of paraffin rich naphthas for the production of high volume yield of gasoline product of desired high ON quality in combination with gasiform product rich in LPG product material.

It is a still further object of this invention to selectively upgrade paraffin rich naphthas to an aromatic rich product and gaseous material rich in LPG.

Other objects and advantages of this invention will become more apparent from the discussion hereinafter presented.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a set of curves illustrating the unique characteristics of this invention.

FIG. 2 is a schematic drawing illustrating an adaption of this invention.

SUMMARY OF THE INVENTION

In accordance with this invention, one or more of the above objectives is accomplished by establishing specific catalytic reaction methods and systems arranged to provide a particularly selective and desirable combination of chemical transformations to occur. The new selective upgrading operation of this invention hereinafter described will therefore, and for convenience, be termed an octane cracking operation, referring to the inverse relationship between component octane and component conversion which exists uniquely for the admixture.

The octane cracking operation of this invention comprises contacting a hydrocarbon stream having a substantial naphtha boiling range fraction material for the preferred composition with at least two distinctly different catalyst compositions, comprising a platinum type reforming catalyst on the one hand, employed in cooperation with a n-paraffin selective conversion catalyst differing substantially from the platinum type reforming catalyst in chemical composition, structure and purpose. The selective conversion catalyst employed herein is characterized in one aspect by a highly selective ability to convert low octane paraffin hydrocarbons in admixture with other hydrocarbons to lower molecular weight saturated gasiform product materials when operating under the octane cracking operating conditions herein described as regards the presence of hydrogen, pressure, temperature, vapor residence time, and catalyst residence time. Furthermore, the selective conversion catalyst and operating conditions employed provide conversion of low octane paraffins to saturated products substantially without the production of olefinic products, whereby continued, regeneration-free operation is possible for the processing of from about 300 to about 300 or more volumes of naphtha per volume of catalyst. Therefore, the present invention provides on the one hand a gasoline upgrading process wherein the plurality of reactions occurring to components in the naphtha feed are selectively altered in a direction so that reactions resulting in loss of liquid product are now shifted to more selectively involve the lower ON components. Thus, desired target ON are attainable with even a higher than usual desired product yield. On the other hand, the upgrading process of this invention permits the preparation of aromatic concentrates and saturated gasiform products under conditions allowing long-term on-stream time in, for example, a fixed bed operation.

In the octane cracking operations contemplated by this invention a naphtha charge material boiling in the range of from about C_5, and preferably from about C_6, up to about 380°F. or higher is passed, at least initially with added hydrogen, in contact with a platinum type reforming catalyst A mixed with a shape selective conversion catalyst B at a concentration of about 20 % to 50 % by weight catalyst A, the balance being shape selective conversion catalyst B.

This mixture of reforming catalyst A and shape selective cracking catalyst B increases the octane limits

achievable by the use of these two catalysts in combination with each other as contrasted with using such catalysts alone in separate beds. When the catalysts are employed in separate beds such as with catalyst B following catalyst A, rather than in a mixture as per this invention, the shape selective cracking catalyst or catalyst B cracks only those normal paraffins present in the reformate. This cracking limitation is due to the limited pore size of catalyst B which will only allow entry of such straight chain hydrocarbons therein. Such an operation of successive catalyst beds has an "octane ceiling" as the amount of the lower octane normal paraffins cracked out of the reformate or virgin naphtha is limited by the total amount of normal paraffins in the feedstock. With the mixing of shape selective cracking catalyst and platinum reforming catalyst, as the shape selective cracking catalyst removes normal paraffins from the feed causing a deficiency of this isomer, the reforming type A catalyst will isomerize some of the iso-paraffins in the feed to normal paraffins. This additional normal isomer can then be cracked out of the feedstock by the type B catalyst. The isomerizations taking place over the platinum reforming catalyst have a certain rate as does the shape selective cracking of normal paraffins. It has been found that mixing platinum reforming catalyst and shape selective cracking catalyst in the proportions specified above have an unusual and unexpected cooperative effect in that the cracking and isomerization reactions take place at such respective relative rates as to maximize the octane activity achieveable with this combination of catalysts. The "octane ceiling" of the product is thus raised to higher levels.

This mixture of reforming and cracking catalysts does not convert all iso-paraffins to normal paraffins from whence they are cracked to propane gas. It is primarily only those paraffin chains having a single methyl group attached to the main chain (monomethyl paraffins) which are converted to normal paraffins. The rates of isomerization of the more complex iso-paraffins to either normal paraffins or to monomethyl substituted materials are very low in comparison. In fact the relative isomerization rates of higher octane isomers to lower octane isomers seems to be inversely proportional to their octane numbers at least in the mixed catalyst system of this invention. It is this selective isomerization coupled with the selective cracking which is believed to produce increased octane product at higher yields than were heretofore achievable.

Platinum type reforming catalyst referred to herein as catalyst A for convenience, may be selected from a number of the known reforming catalysts of the prior art. They may include as a substrate, for example, alumina in the eta, chi or gamma form and mixtures thereof in combination with a noble metal. The platinum type metal on this substrate includes, for example, the metal series which includes platinum, palladium, osmium, iridium, ruthenium, rhodium alone and in mixtures. Generally, the major portion of the catalyst will be alumina and may comprise as much as about 95% by weight or more of the catalyst. Other components may be combined with the alumina carrier, such as the oxides of silicon, magnesium, zirconium, thorium, vanadium, titanium, boron or mixtures thereof. The platinum-alumina combination, either with or without one or more of the above-listed components such as silica, etc., may also be promoted with small amounts of halogen such as chlorine and fluorine, in amounts ranging from about 0.1% up to about 5 by weight. Generally, less than about 3% of halogens is employed with the platinum type catalyst. In a preferred embodiment, the reforming catalyst carrier material is a relatively high surface area material, preferably an eta alumina material of at least about 100 square meters per gram. Preparation of the type A catalyst may be accomplished by many different procedures described in the prior art. In one procedure an alumina carrier material is impregnated with the acid or salt of one or more of the herein-described platinum type metal components in amounts that range from a fraction of a percent up to about 1% by weight. Generally not substantially more than about 0.6% by weight of platinum is employed.

It is to be understood that a naturally occurring or synthetically prepared alumina with or without silica may by employed as a carrier material or support for the platinum type reforming catalyst. Preferably, the platinum-alumina catalyst employed comprises a high surface area material such as an eta base alumina discussed above. Before use, the high surface area platinum catalyst may be reduced in a hydrogen atmosphere and maintained preferably in a relatively dry moisture-free atmosphere before being put on-stream. Desiccated conditions for the catalyst are preferred since it has been found that for a given moisture and certain related temperature level a relationship exists which decreases the desired high surface area of the catalyst and has a simultaneous deactivating effect on the catalyst. Accordingly, it is preferred to employ relatively dry conditions in the process of this invention. This is particularly true, however, when carrying out this process employing relatively low pressure reforming conditions below about 400 p.s.i.g. and not substantially above about 200 p.s.i.g.

It is understood that the term "platinum type reforminng catalyt" or type A catalyst designates a catalyst which performs the well-known reforming reactions of hydroisomerization and aromatization under conditions creating a negligible concentration of olefins in the effluent product. While the above described catalysts are examples of this class, the platinum type catalyst term as used in connection with this invention should not be construed to be restricted to a particular chemical composition per se, as regards the platinum type metal nor the base or support material.

For example, it is contemplated using as a "platinum type reforming catalyst," compositions which may include a crystalline aluminosilicate base substance having a pore structure sufficiently large to allow passage therein of substantially all molecules contained in a naphtha charge, and associated with a dehydrogenation element of the transition metal series, and having its acidic catalytic activity adjusted to a relatively low level which is characterized by an alpha value of less than 1.0 and preferably of about 0.01 to 0.1. The alpha scale and measurement has been described in publication in the Journal of Catalysis, vol. 4, No. 4, August 1956, pages 527 to 529. In the case of catalysts with associated dehydrogenative metal, the alpha test is carried out after suitable poisoning of the meal activity as per advance contact with a sufficiently large amount of hydrogen sulfide. In the above example, the prescribed low level of acidic activity may be achieved by providing a controlled and relatively high concentration of al-

kali metal ion concentration within the aluminosilicate.

The shape selective conversion catalyst, type B catalyst, is a porous solid particle material having a majority of its pores of substantially uniform small dimensions, large enough to allow uptake and egress of normal paraffin molecules, such as, for example, n-hexane, but too small to allow a similar uptake of either branched chain or cyclic hydrocarbons, such as, for example, methylpentane, cyclohexane or benzene. Accordingly, the type B shape selective catalytic material is a highly porous material wherein a substantial majority of its pores are of a uniform dimension in the neighborhood of about 4.5 to about 6.0 Angstrom units effective diameter. Type B catalyst is essentially a shape selective hydrocracking catalyst substantially provided with in-pore acid activity cracking sites and in-pore catalytically effective hydrogenation-dehydrogenation sites. In some cases, one of the two functions or types of catalytic sites may be associated with the molecular shape selective material but externally located. The hydrogenation-dehydrogenation component introduced during manufacture of the catalyst, involves one or more of the elements known as the transition metals. Preferably, one or more of the elements of nickel, cobalt, molybdenum, iron or of the platinum or palladium family are employed. One or more of the elements employed may also involve an element of the higher molecular weight transition series which have hydrogenation-dehydrogenation activity, such as tungsten.

In one embodiment, the catalytically active solid material comprising type B catalyst is a modified zeolite oxide, having a crystalline, rigid and uniform cavity structure of the aforementioned dimensions. Examples are to be found among a number of aluminosilicate minerals, and among synthetically prepared crystalline aluminosilicates which have structures analogous to, and sometimes differing from minerals known to occur naturally: chabazite, gmelinite, stilbite, erionite, offretite, epistilbite, desmin, zeolites S, T, A, ZK–4, ZK–5 and others. It is to be noted that terms erionite and offretite will be considered to be identical in meaning as regards reference to the same or closely equivalent structure mineral form, in accordance with the findings reported in Mineralogical Magazine, vol. 33, pp. 66–67, 1962, by M. H. Hey and E. E. Fejer entitled "The Identity of Erionite and Offretite".

Other porous materials may be employed provided they possess the above described characteristic pore dimensions. Thus, for example, porous carbons can be employed which have undergone suitable treatment to convey to them pore dimensions in the desired range of from about 4.5 to about 6.0 Angstroms.

Introduction of one or more of the metallic catalytic component may be achieved either by processes allowing this component to penetrate the existing or preformed porous solid and be fixed therein, or by formation on synthesis of the porous solid itself in a compositional environment which contains the desired metallic component in suitable form so as to be incorporated in the porous structure in the formation of the porous solid or in the course of its modification to the desired pore structure.

In another aspect of this invention, molecular sieve like carbons can be used to advantage which are produced by heat treating high polymer materials such as polyvinylchloride, polyvinylidine chloride, polystyrenes, polystyrenes containing halo-, sulfonate or other groups on the aromatic nuclii, polymers from monomeric units containing elements or groups comprising elements from Groups VI and VII of the Periodic Table to pyrolitic temperatures. Thus, for example, suitable porous carbons can be produced from vinylidene chloride polymers at high temperature. Methods have been described by Dacey and Thomas in the Transactions of the Faraday Society, vol. 50, 1954, beginning with p. 740; and by Lamond, Metcalfe and Walker, in Carbon, vol. 3, 1965, beginning with p. 59. Other organic polymers may also serve as starting materials such as soft coals, anthracite and other carbonaceous solids that can be converted to suitable porous solids similar to the base material used for the B type catalyst herein described.

It is preferred to impart the type B catalyst with certain magnitudes of acid catalytic activity. For example, when LPG product is preferred over methane, the preferred acid activity will have an alpha value in excess of 10. This process employs the catalyst at a temperature of 900°F. or higher, a more preferred acidity level is that which will account for between 5 and 300 alpha; for operation at about 800°F., above about 500 alpha; for operation at about 700°F., above about 2000 alpha. A very practical method of assaying the acidity in terms of alpha value, of the type B catalyst is by testing its n-hexane cracking activity under prescribed conditions in the absence of hydrogen. Such a procedure in fact constitutes the procedure of the alpha test, as outlined in a previously cited publication.

In order to achieve the required activity level without exceeding the preferred range, for purposes of operating stability, the following types of catalysts or procedures for making same, constitute preferred examples:

Suitable crystalline aluminosilicates, such as desmine, ZK5, described in U.S. Pat. No. 3,140,251, erionite, chabazite, and others, may be prepared having an appreciable fraction of cation sites occupied by hydrogen — or hydrogen precursor cationic form such as ammonium, prior to any calcination — an appreciable fraction by transition metal ions, and the balance by one or more of the alkaline metals or alkaline earth metals.

For example, erionite may be acid treated to remove initial cations and impurities, and subsequently base-exchanged with a solution of Ca-ion, or Mg-ion, or mixture therefore until most of the cation exchange capacity is satisfied by that ion. The transition metal ion may be introduced simultaneously, or by a subsequent exchange process. A more exacting control of the catalyst quality may be achieved by exchange of the zeolite simultaneously with a solution comprising at least one of the ions of each of the two groups comprising in the first group Mg^{2+}, Ca^{2+}, Sr^{2+}, and in the second group H^+ and NH_4^+, in such proportion as to result in an ultimate product of desired acidity. In every case, the transition metal may also be introduced as described above, that is before, simultaneous with, or after the aforesaid exchange. Extended calcination is indicated for increasing the acidity of NH_4^+ containing preparations.

It is also possible to control the acidity of catalyst type B prior to use in the process of this invention, or in situ, if overactivity is to be reduced, by contacting limited amounts of ammonia or ammonia producing volatile components with the type B catalyst charge.

DESCRIPTION OF PREFERRED EMBODIMENTS

In accordance with the invention herein described, a naphtha boiling range charge material is contacted with a mixture of catalysts A and B under relatively typical platinum reforming conditions, the B catalyst representing about 20 to about 50 weight percent of the total catalyst bed. As illustrated in FIG. **1**, such a relative concentration maximizes the octane increase produced by such a catalyst composition under given operating conditions. Moreover, as is more fully described by Tables 1–3, such a particular catalyst relative concentration has the remarkable attribute of selectively "cracking out" of the charge stock those hydrocarbon components having lower octane values and converting these to LPG.

The operating conditions employed in the process embodiments of this invention are selected such that the mixture of catalysts A and B are exposed to the following relatively typical reforming conditions: a temperature of about 800° to 1020°F and preferably in the range of about 850° to 930°F; a liquid hourly space velocity of about 0.1 to 20 and preferably from about 2.0 to 10.0; a pressure of about 150 to 600 psig, preferably in the range of about 200 to 400 psig; and a hydrogen-hydrocarbon ratio of about 2 to 20 and in a preferred embodiment about 4 to 8. In a preferred embodiment, the minimum research octane increase of the petroleum naphtha or reformate thereof across a reactor containing a catalyst mixture as defined by this invention is about 6 to 9.

The selective conversion involving the catalyst of type B, was found to proceed under conditions of pressure and temperature which are regarded as either hydrogenative or aromatizing in the thermodynamic sense. Therefore, the operation may be effected at lower temperatures and higher pressure than is generally allowable in the normal reforming operation which is limited to the range of aromatizing conditions, that is for an equilibrium which favors aromatics in the reversible system, naphthenes $\rightleftarrows$ aromatics. In addition, the temperature of operation applicable to contact with type B catalyst will depend on and be correlated to the acidity of the B catalyst composition. That is, if it is prepared to contain much acidity internally, or is admixed with external acidic solid, operation at a relatively lower temperature can be achieved.

In any of the arrangements above discussed using crystalline aluminosilicate zeolite material for the type B catalyst, it is particularly preferred to utilize a zeolite having a silica/aluminum ratio not less than about 2.0 and preferably the ratio should be at least about 3.0.

It should be noted also that the invention involves a cooperative hydrogen economy between the different parts of the conversion process in that hydrogen consumed by the mechanisms operative on catalyst B is produced in and derived from the conversion events over catalyst A. For the more active type B catalysts a larger amount of reforming catalyst (perhaps as high as 70% by weight) is required to effect this cooperative effect.

Shape selective conversion catalysts type B suitable for use in the method of this invention were prepared as follows:

Catalyst B was prepared from a naturally occurring zeolite (erionite) of about 4 to 6 Angstroms pore size. One part by weight of the crystalline aluminosilicate zeolite was base-exchanged for about 2 hours at room temperature with about ten (**10**) parts by weight of 5% NH_4Cl solution. This treatment was repeated three additional times for a total time of the order of about 20 hours with the last treatment being for about 16 hours duration. The residue obtained from this NH_4Cl treatment or base-exchanged step was thereafter water washed to remove chloride from the residue and then filtered. The filter cake thus obtained was refluxed with about 25 parts (wt.) of 0.5 N nickel acetate solution for about 10 minutes and then filtered. The filtered solids or residue was then again water washed. The residue thus obtained was dried, pelleted, crushed to about 30/**60** mesh size particles and then air calcined at a temperature of about 1000°F. for about 16 hours. A sufficient quantity of the calcined catalyst was placed in a reactor and H_2 reduced or activated for about 4 hours at a temperature of about 950°F. and a pressure of about 400 psig. while maintaining fresh flow of H_2 rich gas at about 6 s.c.f./h.

EXAMPLES 1–12

A C_6-290°F light reformate having a C_5^+ research octane number of approximately 76 (no lead addition) was contacted within a reactor with a mixture of (1) a typical reforming type A R–16 reforming catalyst and (2) a shape selective type B cracking catalyst comprising an activated erionite. The two were mixed so as to produce a mixture containing 0%, 15%, 35%, 60% and 85% by weight respectively of the type A catalyst. The test conditions for the examples were as follows: A hydrogen to hydrocarbon molar ratio of about 6:1; a pressure of approximately 250 psig and 9 LHSV. Three runs were made with each catalyst mixture at 880°F., 900°F. and 920°F. respectively. The clear research octane values of the thus treated chargestock are shown in FIG. **1**.

EXAMPLES 13–19

A reformate whose hydrocarbon components are as noted in col. 1 of table 3 was reacted over the catalyst mixtures as defined in table 1 at about 400 p.s.i.g. and a hydrogen/hydrocarbon ratio of about 5.1/1 and at a liquid hourly space velocity of about 2.0.

The reaction products were collected in a heated dropout pot at 400 p.s.i.g. and the lighter products condensed in a two stage condenser where the liquid was collected at ambient temperature and the vapors passed through a reflux condenser maintained at about −20° to −18°C. The liquids were combined, weighed and analyzed with a chromatograph prior to being analyzed for research octane number. Table 1 shows a liquid yield summary and table 2 shows the conversions of normal and mono-substituted hydrocarbons. As illustrated by examples 15 and 19, a mixture of 20% by weight of type A reforming catalyst combined with 80% type B catalyst extends the octane ceiling for a 92 ON mid-continent reformate at a temperature of 900°F from 99.8 ON (research octane without lead addition) for 100% type B catalyst to 104.9 ON (again research octane without lead.)

Comparing the conversion of normal and mono-substituted hydrocarbons as shown in table 2, it is noted that the present conversion favors maximum octane number improvement (mono-C_7 conversion > mono-C_6 conversion > mono-C_5 conversion) and is shown at higher temperatures and increasing concentration of type A reforming catalyst.

TABLE I

EXAMPLE NO.	13	14	15	16	17	18	19
	LIQUID YIELD SUMMARY						
		100% TYPE B		5% TYPE A 95% TYPE B		20% TYPE A 80% TYPE B	
Temperature	700°F	800°F	900°F	800°F	900°F	800°F	900°F
Product							
C_5^+ yield, vol. %	94.3	86.2	82.5	81.8	74.8	81.4	67.9
O.N., R+O	94.6	98.1	99.8	99.0	102.3	99.1	104.9
$(C_1 + C_2)/(C_3 + C_4)$	.053	.115	.526	.147	.512	.125	.325

TABLE 2

CONVERSIONS OF NORMAL AND MONO-SUBSTITUTED HYDROCARBONS

EXAMPLE NO.		13	14	15	16	17	18	19
Reaction Temperature		700°F	800°F	900°F	800°F	900°F	800°F	900°F
Conversion of	(wt.% in feed)							
n-octane	(1.14)	10.6	62.2	100.	98.2	100.	96.6	99.7
n-heptane	(2.94)	45.6	91.5	100.	100.	100.	99.3	99.3
n-hexane	(4.34)	41.5	95.0	100.	100.	99.5	99.1	98.6
n-pentane	(4.20)	63.1	72.6	95.0	90.0	99.0	76.9	93.1
2MH & 3MH	(6.34)	*	*	*	12.5	32.5	20.0	68.3
2MP & 3MP	(6.97)	*	*	*	12.1	32.0	15.9	51.9
isopentane	(4.40)	*	*	*	0.0	6.8	3.0	13.9
other hydrocarbons	(69.17)	0.0	1.3	2.7	2.5	3.3	3.3	10.2
total normals + monosub. cracked**								
total crack products		1.0	.83	.77	.81	.82	.79	.70
Total C_4 – yield		5.7	14.6	17.2	18.1	21.9	18.9	30.4

*Lumped with other hydrocarbons
**n-octane not included

TABLE 3

REACTION PRODUCTS, FULL RANGE REFORMATE (92.0 R+0)
400 psig, 2 LHSV, $2H_2$/HC MOLAR RATIO

Example No.	Feed	13	14	15	16	17	18	19
Catalyst		100% TYPE B			5% TYPE A 95% TYPE B		20% TYPE A 80% TYPE B	
Temperature	400°F	700°F	800°F	900°F	800°F	900°F	800°F	900°F
Methane	—	0.11	0.45	2.30	0.55	2.05	0.42	1.54
Ethene	—	0.06	0.00	0.00	0.03	0.10	0.03	0.08
Ethane	—	0.20	1.03	3.63	1.73	5.28	1.64	5.83
Propene	—	0.00	0.20	0.27	0.20	0.06	0.18	0.19
Propane	—	3.15	8.74	9.22	11.39	13.17	10.53	17.44
Isobutane	0.51	1.02	1.33	1.07	1.93	0.98	2.00	3.18
Butane	1.97	1.20	2.59	0.71	2.24	0.30	4.06	2.13
2-Methylbutane	4.40	2.22	4.25	3.62	4.41	4.10	4.27	3.79
Pentane	4.20	1.55	1.15	0.21	0.42	0.04	0.97	0.29
2,2-Dimethylbutane	0.59	0.57	0.94	0.41	0.98	1.07	1.02	1.09
2-Methylpentane	4.24	4.48	3.78	3.63	3.75	2.91	3.61	2.13
3-Methylpentane	2.73	2.87	2.45	2.35	2.38	1.83	2.25	1.22
Isohexanes	2.48	0.62	1.37	1.67	1.58	1.25	1.45	1.27
Hexane	4.34	2.15	0.22	0.00	0.00	0.02	0.04	0.06
2,4-Dimethylpentane	1.51	1.64	1.37	1.30	1.58	1.14	1.90	0.57
3,3-Dimethylpentane	0.22	0.23	0.20	0.21	0122	0.20	0.27	0.15
2,3-Dimethylpentane	0.95	1.00	0.86	0.88	0.81	0.64	0.80	0.36
2-Methylhexane	2.81	3.00	2.62	2.61	2.46	1.89	2.27	0.85
3-Methylhexane	3.53	3.77	3.33	3.42	3.09	2.39	2.80	1.16
n-Heptane	2.94	1.60	0.25	0.00	0.01	0.00	0.02	0.02
n-Octane	1.14	0.96	0.43	0.00	0.02	0.00	0.04	0.01
Benzene	4.54	4.84	4.64	5.66	4.44	5.33	4.14	5.37
Toluene	15.21	16.43	15.52	17.62	14.93	17.13	14.71	16.63
Cycloparaffins	1.59	1.90	1.61	2.00	2.59	1.43	2.65	1.09
Others	39.95	44.47	40.67	36.69	33.47	36.71	37.94	33.59
Mass Balance	98.52	103.90	100.52	98.21	98.51	99.83	97.36	98.33
C_5^+ Yield* wt.%	97.44	94.64	85.96	82.93	81.60	76.05	81.28	70.08
vol.%	97.63	92.82	84.01	80.53	79.82	73.02	79.48	66.31
H_2 Consumption Calc.%	—	0.31	0.42	0.42	0.43	0.39	0.34	0.81
(grams/100 grams feed Meas.%	—	0.08	0.39	0.86	0.20	0.67	0.62	1.38
Liquid Product Octane Number (R+O)	92.0	94.6	98.1	99.8	99.0	102.3	99.1	104.9

*Based on 100% Recovery

Referring now to FIG. 2 by way of example, a process flow arrangement is diagrammatically shown comprising a three reactor (R_1, R_2 and R_3) reforming system, a reformate product separator, a depropanizer tower and a debutanizer tower from which a C_5+ reformate product can be recovered. The naphtha boiling range hydrocarbon feed enters the process by conduit **12,** is combined with a hydrogen rich recycle gas in conduit **4** and passed by conduit **6** to reforming reactor R_1. The naphtha feed may be brought up to reforming temperatures in a suitable heater, not shown, either before or after admixture with the hydrogen rich recycle gas, so that it has an inlet temperature sufficiently high to provide the endothermic reaction heat required in reactor R_1. The combined stream of hydrogen and hydrocarbon flows in series through reactor R_1, conduit **8,** heater **10,** conduit **12,** reactor R_2, conduit **14,** heater **16,** conduit **18** and reactor R_3. In this arrangement reactor R_3 houses a mixture of a platinum type reforming type A catalyst and a shpae selective type B hydrocracking catalyst.

In reactor R_3, the total reformate product from reactor R_2 moves into contact with the mixed upgrading catalyst of this invention under conditions sufficient to obtain the conversion of hydrocarbons described above. The total product effluent of reactor R_3 is thereafter passed to a suitable separator vessel **24** by conduit **20** containing heat exchanger **22.** In separator **24,** a hydrogen recycle gas stream is separated from the remaining upgraded reformate product and removed by conduit **26** for recycle to conduit **4.** A portion of this recycle gas may be withdrawn by conduit **28.** The remaining reformate product is removed by separator **24** by conduit **30,** passed through heat exchanger **22** and then through conduit **34** to a depropanizer tower **36.** In tower **36,** C_3 and lighter hydrocarbons are separated and removed by conduit **38** from the reformate product. The depropanized effluent is then passed by conduit **40** to a debutanized tower **42.** Butane rich gas is recovered from tower **42** by conduit **44** and a C_5+ upgraded reformate rich in aromatics and high octane number branch chained hydrocarbons is recovered by conduit **46.** The sensible heat of the product stream leaving reactor R_3 may be utilized to preheat the fresh naphtha feeds passed to the process by heat exchange in heat exchange **22.**

Having thus provided a general description of the invention and presented several examples in support thereof, it is to be understood that no undue restrictions are to be imposed by reason thereof.

What is claimed is:

1. In the method of upgrading the octane number of a naphtha boiling range hydrocarbon fraction by the sequence of reforming using a platinum type reforming catalyst followed by shape selective conversion of the reformate using a shape selective crystalline aluminosilicate zeolite catalyst having a pore size of 4.5 to 6.0 Å such as to admit only molecules having an effective diameter up to that of normal paraffins; the improvement which comprises utilizing in said shape selective conversion step a catalyst which is a mixture of said shape selective zeolite and about 20 to 50 weight percent of a platinum type reforming catalyst.

2. The method as claimed in claim **1** wherein said shape-selective catalyst is a crystalline aluminosilicate zeolite having a silica to alumina ratio of at least about 2.

3. The method as claimed in claim **1** wherein said shape selective catalyst comprises erionite.

4. The improved method claimed in claim **3** including carrying out said reforming at about 150 to 600 psig, 800 to 1020°F and 0.1 to 20 LHSV; and directly subjecting the product of said reforming to said shape selective conversion.

5. The method as claimed in claim **1** wherein said platinum type reforming catalyst is predominantly an eta alumina based catalyst.

6. The improved method claimed in claim **1** wherein said reforming catalysts consist essentially of at least about 95 weight percent alumina, about 0.1 to 5 weight percent chloride and an effective amount up to about 1 weight percent platinum.

7. The method as claimed in claim **1** wherein said naphtha hydrocarbon fraction is passed over said catalyst mixture in said shape selective conversion step under reforming conditions at a pressure below about 600 psig.

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