

Aug. 26, 1958

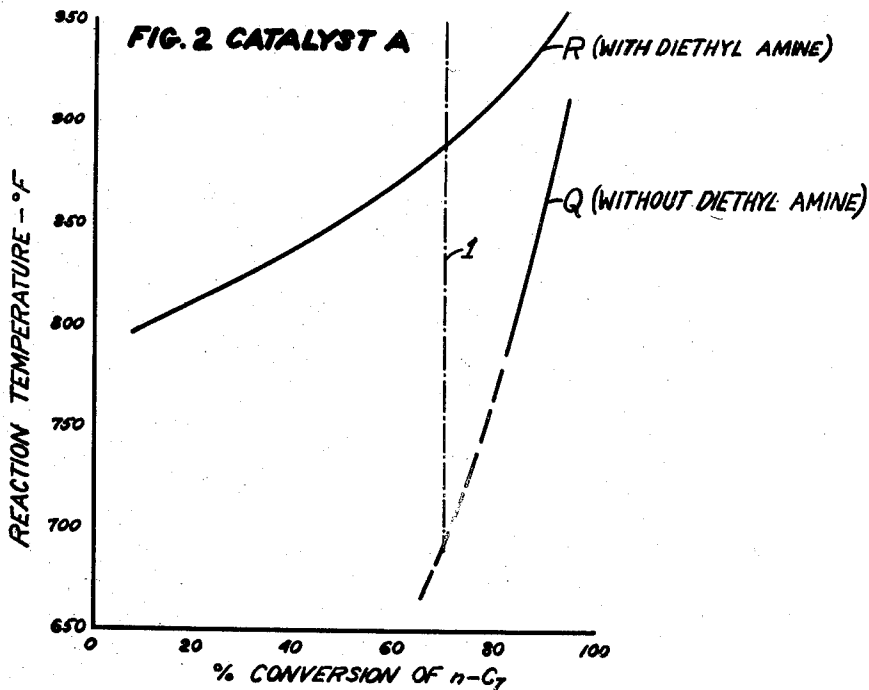
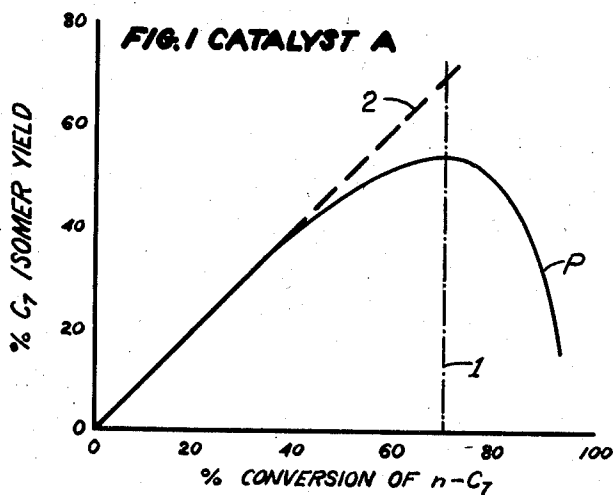
H. B. OGBURN ET AL

2,849,377

CONTROL OF CATALYTIC REFORMING PROCESS

Filed April 16, 1953

4 Sheets-Sheet 1



ATTEST:

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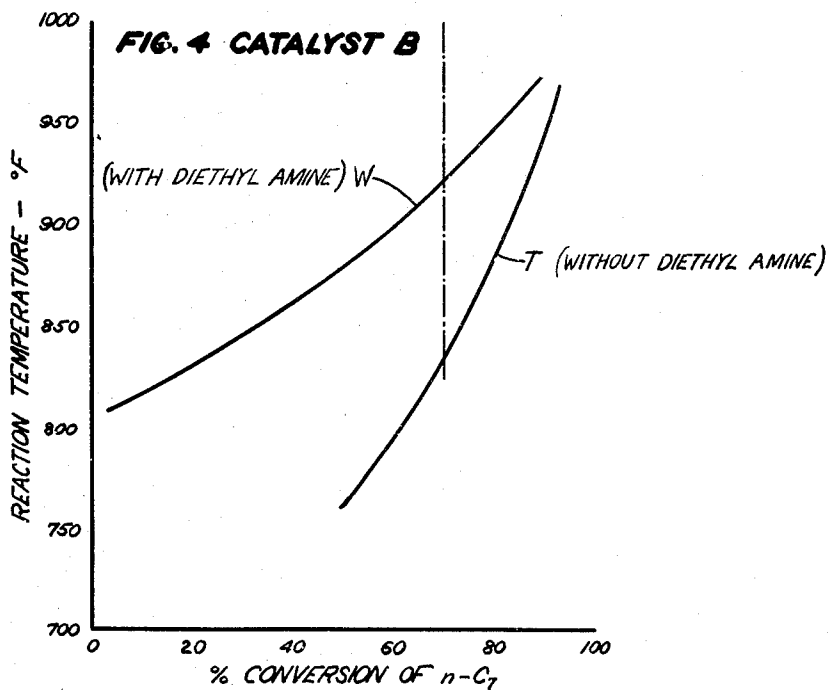
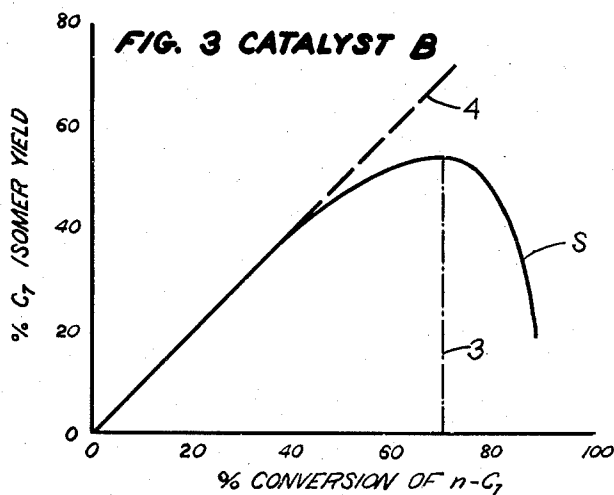
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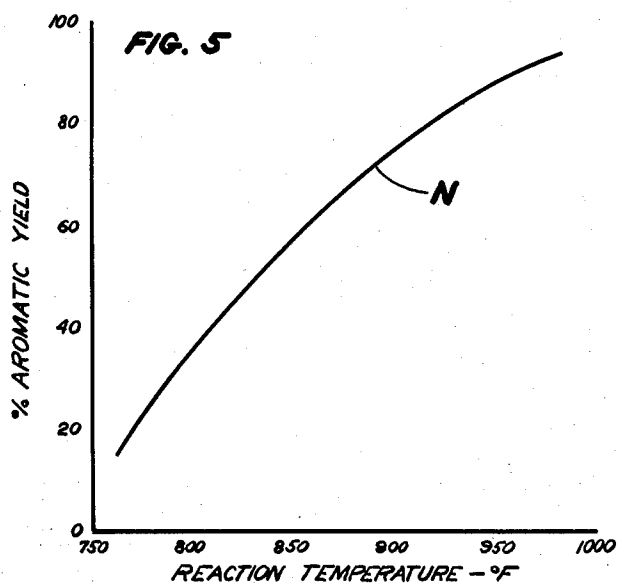
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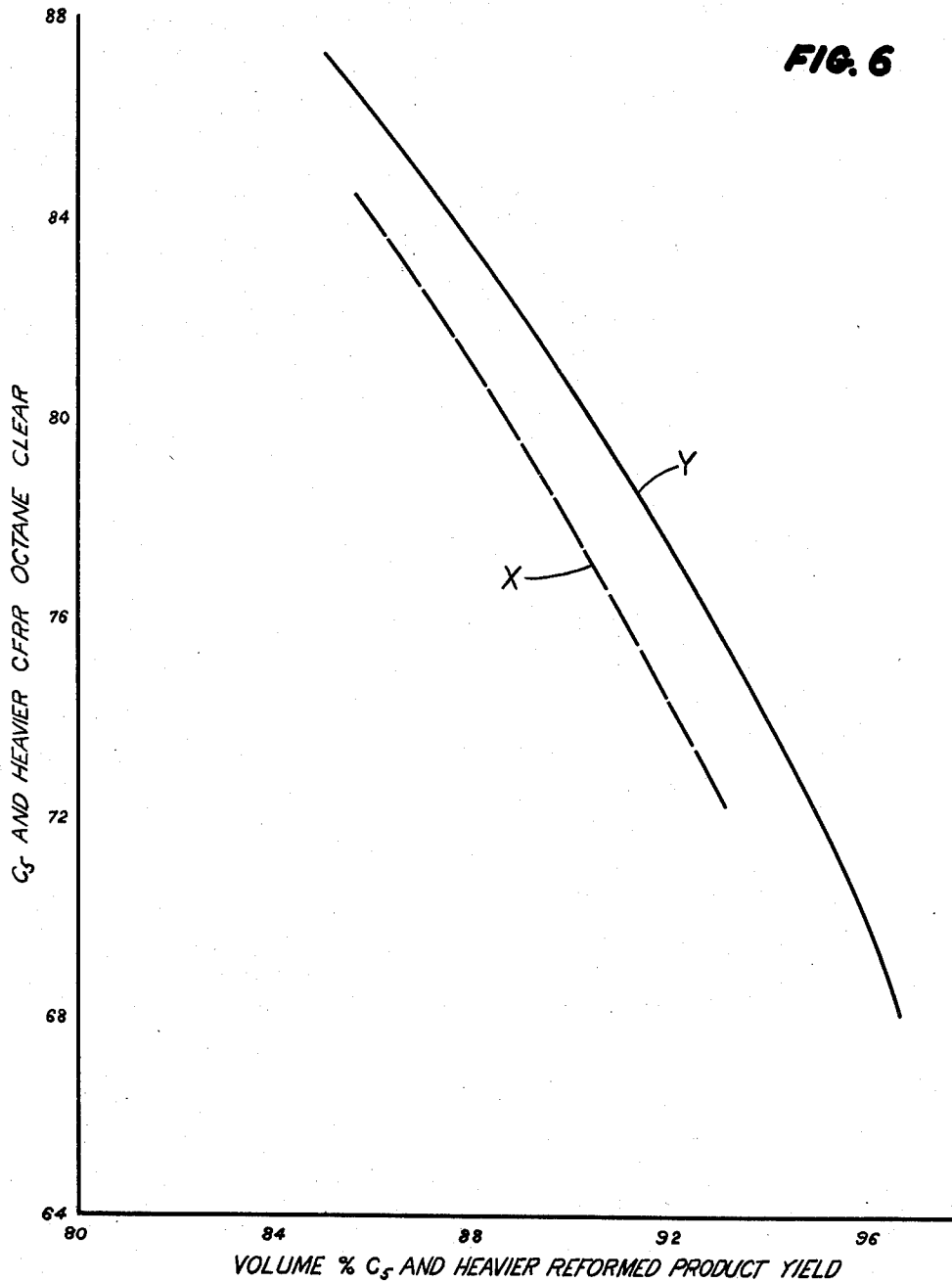
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CONTROL OF CATALYTIC REFORMING PROCESS

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2,849,377

CONTROL OF CATALYTIC REFORMING PROCESS

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Application April 16, 1953, Serial No. 349,122

13 Claims. (Cl. 196—50)

This invention relates to improvements in methods for controlling reactions in catalytic reforming processes and, more particularly, to the control of isomerization reactions in such processes when utilizing a platinum or palladium impregnated acidic metal oxide base catalyst.

Modern refining technology has as one of its primary objectives the efficient and economical production of maximum quantities of high octane gasoline. Until recently, it has been possible to meet the required overall motor fuel octane levels by catalytically cracking gas oil fractions to yield a high octane gasoline component for blending with the lower octane straight run and the thermally cracked or thermally reformed gasoline components to yield a marketable product. The ever-increasing demands for higher octane fuels have rendered untenable this processing method and have resulted in the development of the catalytic reforming processes specifically designed to improve the octane quality with high volumetric recoveries of the relatively low level straight run and thermal gasoline fractions.

These straight run and thermal gasoline fractions are composed of straight chain, slightly branched chain, and cyclic paraffins and olefins, all of which have relatively low octane values together with only minor amounts of aromatics. In order to increase the octane value of the non-aromatic compounds in these low octane fractions, it is desirable to isomerize the straight chain and slightly branched chain hydrocarbons to highly branched chain compounds, and to isomerize the cyclic saturated compounds (naphthenes) to six carbon ring structures to be dehydrogenated to the corresponding aromatics, the dehydrogenation reaction being especially important since the aromatics produced contribute markedly to the over-all octane improvement. Another desired reaction is the conversion of paraffins to aromatics by dehydrocyclization. Finally, and of considerable importance is the selective cracking of the high molecular weight hydrocarbons to produce high yields of normally liquid products without the formation of large amounts of gas and coke. Although many catalysts have been proposed which are useful in promoting some of these reactions, only certain of the platinum or palladium impregnated acidic metal oxide component catalysts are known to be capable of successfully promoting all of the desired reactions in a ratio which will give the greatest octane improvement with the lowest loss in yield. One example of such catalyst contains silica and alumina as the metal oxide component. Other metal oxide components which may be impregnated with platinum or palladium to produce reforming catalysts suitable for use in this invention include: alumina, silica-zirconia, silica-alumina-zirconia, silica-magnesia, silica-alumina-magnesia, silica-thoria, silica-alumina-thoria, alumina-thoria, and similar oxide combinations. These metal oxide components, in general, are active catalysts for the cracking of hydrocarbons. Their preparation and properties have been widely published both in patents and in technical literature, and because of which this information will not be reiterated here.

2

Although these reforming catalysts have the ability to promote the several reactions set forth, they are particularly valuable since they promote the isomerization of naphthenes into hydrocarbon structures which are more easily dehydrogenated into aromatics. For example, in the C_6 hydrocarbon fraction of a straight run naphtha, methyl cyclopentane predominates over cyclohexane at a ratio generally of about 2 to 1. Consequently, it is extremely desirable for maximum production of aromatics to convert the methylcyclopentane into cyclohexane which can be dehydrogenated to produce the desired aromatic, i. e., benzene. These catalysts promote both of these reactions quite readily.

The ability of a catalyst to promote the isomerization of methylcyclopentane into cyclohexane is probably the most critical test for a reforming catalyst, since this isomerization is difficult to promote without degrading side reactions. If a catalyst will promote this reaction, it will also promote the isomerization of dimethylcyclopentanes into methylcyclohexane and similar analogous isomerization reactions.

It is necessary when using these catalysts, however, to have present rather large amounts of hydrogen, in order to maintain the catalyst in a clean condition and free of coke and carbonaceous deposits which would substantially deactivate the catalyst if allowed to accumulate. Since there is a net production of hydrogen in the over-all reforming reaction, there is no serious problem with respect to hydrogen supply; however, to make the hydrogen effective, superatmospheric pressures must be used or, in other words, the hydrogen partial pressure must exceed one atmosphere.

The dehydrogenation reaction is one of the most rapid of the reforming reactions and, therefore, under most operating conditions, equilibrium can be reached between the naphthenes and the aromatics. Since, however, the volume of the products exceeds the volume of the reactants, the reaction is of course effected by pressure in the reverse direction—that is, the formation of aromatics is decreased as the pressure is raised at constant reaction temperatures. In addition, it is well-known that at a constant pressure, as the reaction temperature is increased, the equilibrium shifts in the direction of higher aromatic concentrations. It follows, therefore, that since it is highly desirable to have the equilibrium as far as possible in the direction of maximum production of aromatics and, since superatmospheric pressures must be used, higher temperatures must also be employed.

To summarize the foregoing: (a) hydrogen at superatmospheric pressures is necessary to maintain the reforming catalyst in a clean condition, (b) dehydrogenation of naphthenes to aromatics produces hydrogen and in addition furnishes an important increment of octane improvement, (c) equilibrium considerations require the use of elevated temperatures to produce the maximum quantities of aromatics and hydrogen at the superatmospheric pressures, and (d) isomerization reactions must be promoted to a maximum extent within the same range of conditions where maximum aromatic formation is realized. When all four of these requirements are met simultaneously in a reforming process, that is, when all the desired reactions are in proper ratio one to the other, there results the optimum yield-octane relationship for the process.

Consequently, the efficiency of a reforming process may be measured by determining the isomerization selectivity of the catalyst under the physical conditions imposed by equilibrium considerations to produce maximum aromatics. The term "isomerization selectivity" may be defined as the ratio (expressed in percent) of the percentage of isomer yield to the percentage conversion of a particular hydrocarbon charged. For example, if n-heptane were the hydrocarbon charged and a 40 percent yield of C_7

isomers were obtained with a 40 percent conversion of the n-heptane feed, the isomerization selectivity would be 100 percent. If, however, when 75 percent of the n-heptane is converted a yield of only 65 percent C₇ isomers based on the charge is obtained, the isomerization selectivity is approximately 87 percent. Therefore, the optimum conditions are those wherein a maximum yield of isomers is obtained with the highest possible isomerization selectivity. Since conversion is a function of reaction temperature, it then becomes possible to adjust the reaction temperature within a range corresponding to a range of conversion levels in which the highest isomerization selectivity is maintained and maximum isomer yield realized.

In studying the reforming efficiency of these catalysts, it has been found that the isomerization selectivity for the isomerization of naphthenes remains at a maximum (100 percent) to a higher conversion level than the isomerization selectivity for the isomerization of straight-chain paraffins of the same molecular weight range as the naphthenes. Expressed in other words, it is possible to maintain maximum isomerization selectivity for naphthene isomerization to higher reaction temperatures than for maximum straight chain paraffin isomerization selectivity.

It becomes apparent from the foregoing that the reforming reaction temperatures must be chosen with regard to the straight chain paraffin isomerization selectivity rather than with regard to the naphthene isomerization selectivity and, since high temperatures are required for the dehydrogenation reaction, the problem becomes one of raising the restricting temperature corresponding to the desired high straight chain paraffin isomerization selectivity into the range where maximum aromatic formation can be obtained by the dehydrogenation reaction.

In U. S. Patent No. 2,550,531, catalysts of the platinized silica-alumina type were used. However, the base was treated prior to platinization to lower its surface area and thereby to permit an increase in the temperature range at which high paraffin isomerization selectivity is obtained with the finished catalyst, so that at the elevated temperatures required for aromatic formation there will not be an appreciable loss in paraffin isomerization reaction selectivity with the attendant loss in yields of isomer products. Thus, according to the patent, essentially the proper ratio between the various reforming reactions is obtained by adjusting the surface area of the catalyst base.

According to the present invention it is also possible to bring the various reforming reactions into proper ratio or balance, particularly when using platinized acidic metal oxide base type catalysts, by introducing into the reaction zone ammonia or compounds which will readily yield ammonia under processing conditions. The introduction of ammonia or its equivalents permits the use of the elevated temperatures required for maximum aromatic formation while retaining high isomerization selectivity for paraffins at maximum isomer yields. This discovery offers a novel and selective method of controlling reforming processes.

In order that the invention may be more readily understood several applications will be described, it being understood that there are many other situations peculiar to particular reforming problems where the use of the invention is also advantageous.

Reforming catalysts of the platinized acidic metal oxide base type are particularly useful since they require only infrequent replacement or regeneration. It is recognized, however, that over relatively long periods of use their activity for promoting the various reforming reactions in proper ratio may change and also in order to compensate for this change in activity, it may be necessary to alter the process conditions in the direction of increasing severity. This is most frequently accomplished by increasing the temperature of the reaction. The operating temperature cannot be increased indefinitely, however, since ultimately the various reactions occurring will be put out of the desired balance, that is, the isomerization selectivity of the catalyst will deviate greatly from the desired high level

with the result that relatively large amounts of normally gaseous hydrocarbons will be produced. It has been found that if ammonia, or any of its equivalents, is introduced into the reaction zone, and by varying the amount in a manner which will be described, it is possible to extend greatly the operable temperature range for the required increased severities while still maintaining the desired balance between the reactions, such balance being characterized by the production of only nominal amounts of normally gaseous hydrocarbons.

Another situation may involve the reforming of a normal boiling range feed stock to produce a reformed product of a particular octane level, such level being dictated by the octane requirements of the total gasoline pool. As often happens, a change in crude supply will require the reforming of a higher boiling hydrocarbon distillate. When this occurs, it is necessary in order to maintain the same octane level in the product, to have a greater octane improvement of the feed which in turn requires more severe reforming conditions. In meeting these increased severity requirements, it might be necessary to operate within a range of conditions making impossible the desired balance of reactions but which, according to the present invention, will be corrected by the introduction of ammonia into the process.

A third application of the invention, somewhat analogous to the preceding situation, involves a change in feed stock wherein the boiling range may change only very slightly, but wherein the hydrocarbon type composition is radically different. For example, should the feed be relatively low in cyclic saturated compounds and relatively high in straight chain paraffinic hydrocarbons, it would be extremely important in order to maintain the desired yield-octane relationship, to control the selectivity of the catalyst so that the straight chain paraffin isomerization selectivity will be maintained. These objectives can be met, even if it is necessary to go to increased operating severities, by the addition of ammonia or its equivalents into the reaction zone.

A further and extremely important application of the instant invention relates to the use of ammonia or its equivalents in catalytic reforming processes employing platinized acidic metal oxide catalysts which have not had their metal oxide bases altered to increase their isomerization selectivity. In the aforementioned U. S. Patent No. 2,550,531, the silica-alumina base was reduced by described methods to a critical surface area prior to platinization in order that the finished catalyst would have high isomerization selectivity within the temperature ranges required for aromatic formation. The teachings of the present invention permit an important improvement to processes employing catalysts of this or similar acidic metal oxide types. Since the addition of ammonia or its equivalents will control the isomerization selectivity of these catalysts, it is unnecessary to modify or alter their metal oxide bases, or merely alter them to a lesser degree than in the aforementioned patent.

In addition when employing ammonia or its equivalents with a platinized acidic metal oxide reforming catalyst which has not had its metal oxide base altered, or altered only to a small degree, the relative activity of the catalyst for promoting the various reforming reactions may change with on-stream time in such direction that the amount of ammonia necessary to maintain isomerization selectivity will decrease. Accordingly, the amount of ammonia mixed with the reactants for most effective reforming over the aforementioned catalysts can be decreased with time until a point is reached where no ammonia addition is required. With further use, additional extensive catalytic activity and selectivity changes may occur in the manner previously outlined, and at this point ammonia may be reintroduced to maintain the desired yield-octane relationship and the operation continued until limiting temperatures are reached, at which point the catalyst must be regenerated or replaced.

It is obvious from the foregoing rather widely diversified applications of the instant invention that various amounts of ammonia will be required. Furthermore, under some conditions of operation the ammonia may be used on a once-through basis; however, the usual practice is one in which recycle hydrogen-rich gas circulation is employed. In the latter case, some of the ammonia introduced into the reaction zone will be contained in the hydrogen-rich gas stream, the amount being determined by the process operating conditions. As another example of a possible recycle system, solvent scrubbing of the effluent gases might be employed to recover the ammonia which then could be recycled with the fresh feed. The ammonia which must be added to any such circulating system is merely the make-up necessary to hold the desired ammonia-to-fresh feed ratio over the catalyst bed. The ammonia-to-fresh feed ratio is dependent upon the particular application and its operating conditions as will be shown hereinafter.

In order to place ammonia and its equivalents on a convenient comparable basis, amounts may be expressed as weight percent nitrogen on a fresh feed basis. It is of course possible to introduce the ammonia either entirely in the fresh feed or entirely in the recycle gas; however, in general, it may be introduced into the reaction system from either or both sources. For example, under certain conditions, the desired weight percentage of nitrogen based on the fresh feed may be 0.6 percent. Of this amount, it may be that as much as 0.5 percent already will be present in or introduced into the hydrogen-rich gas stream, or in another recycle stream in which event the remaining amount of 0.1 percent will be introduced into the system with the fresh feed.

The nitrogen-to-fresh feed ratio is rather small for all of the applications enumerated. In most cases, it will range from about 0.005 percent to about 3.0 percent.

The compounds which are suitable for introduction into the reaction zone according to the present invention include ammonia, ammonium hydroxide, the primary, secondary, and tertiary alkyl amines, alkanol amines, aryl amines, mixed alkyl aryl amines, alkyl diamines, and aryl diamines. Examples of these compounds are: mono-, di-, and tri-methyl amine; mono-, di-, and tri-ethyl amine; mono-, di-, and triethanol amine; mono-, di-, and tri-phenyl amine, phenyl-ethyl amine, phenylene diamine, and similar amines. Although only the lower molecular weight amines have been enumerated, the higher molecular weight members of the various homologous series may be used, since they also will be converted to ammonia under the conditions of the reforming process. In addition to the aforementioned compounds, an extremely large number of other nitrogen-containing compounds are suitable; for example, organic nitrates, nitrites, nitriles, nitroso compounds, amides, imides, ammonium salts (such as ammonium acetate), urea and derivatives thereof, cyanates, isocyanates, isocyanides, quaternary ammonium compounds, nitro compounds, pyridine and derivatives thereof, piperidines, oximes, hydroxyl amine, azo compound, or, in general, any nitrogen-containing compound,

or mixtures of such compounds, which can be converted to ammonia as one of the products under the conditions of reforming is suitable, provided that such compound, or mixtures of such compounds, will not deposit a solid residue on the catalyst. Compounds such as the metallic nitrates, nitrites, and the like are unsuitable since, while they may yield ammonia as one of their conversion products, they have the disadvantage of depositing solid residues on the catalyst.

The following data and appended drawings illustrate the aforementioned effect of ammonia and its equivalents in obtaining the proper balance among the various reactions in a catalytic reforming process:

EXAMPLE I

A blend of 45 percent by weight of normal heptane, 45 percent by weight of cyclohexane, and 10 percent by weight of benzene (such compositions designed to simulate a typical reformer stock) was charged to a reforming unit at 350 p. s. i. g. pressure, a liquid hourly space velocity of 3, a hydrogen to hydrocarbon mol ratio of 10 to 1, at a series of reaction temperatures over two different catalysts (designated A and B) with and without the addition of diethyl amine (the nitrogen containing compound). The hydrogen was not recycled so that the diethyl amine, introduced with the hydrocarbon blend, was used on a once-through basis and in an amount designated as weight percent nitrogen on a fresh feed basis. The diethyl amine was converted to ammonia and appeared in the hydrogen gas product.

Catalyst A was prepared as follows:

A fresh commercial silica-alumina cracking catalyst (approximately 87% silica, 13% alumina by weight) having a surface area of about 425 square meters per gram as determined by the adsorption of nitrogen according to the method of Brunner, Emmett, and Teller, found in the Journal of the American Chemical Society, volume 60, pages 309 et seq. (1938), was used as the metal oxide base. This base was soaked in an excess of 0.0194 molar (as Pt) chloroplatinic acid for approximately ½ hour and then drained and the residual solution removed by centrifuging. The centrifuged material was heated in a closed oven at 230° F. for 24 hours, dried in a stream of nitrogen at 450° F. for 1 hour, and finally reduced with hydrogen at 1000° F. for 16 hours. This catalyst contained 0.28 percent by weight of platinum.

Catalyst B was prepared as follows:

A portion of the fresh commercial silica-alumina cracking catalyst used in the preparation of catalyst A was steamed at 1050° F. and 40 to 45 p. s. i. g. for 18 hours to reduce the surface area from 425 square meters per gram to about 155 square meters per gram. This base material then was soaked in an excess of 0.0247 molar (as Pt) chloroplatinic acid for approximately ½ hour, centrifuged, dried and reduced in the same way as the catalyst A. This catalyst contained 0.27 percent by weight of platinum.

The experimental conditions and results of the various runs are shown in Table I, below:

Table I

Temp. of reaction, ° F.	Catalyst A						Catalyst B					
	Without diethylamine			0.10 weight percent nitrogen ¹ as diethylamine			Without diethylamine			0.03 weight percent nitrogen ¹ as diethylamine		
	Conv. of nC ₇	Percent C ₇ isomer yield	Percent aromatic yield	Conv. of nC ₇	Percent C ₇ isomer yield	Percent aromatic yield	Conv. of nC ₇	Percent C ₇ isomer yield	Percent aromatic yield	Conv. of nC ₇	Percent C ₇ isomer yield	Percent aromatic yield
800	83.4	49.2	24.9	11.8	15.9	45.1	61.5	56.1	27.5	4.5	10.7	46.4
850	87.2	42.3	49.1	42.5	40.3	59.9	72.9	56.8	48.2	22.3	24.2	65.1
900	92.8	23.5	69.9	74.6	49.1	71.9	83.7	42.9	69.7	59.5	45.0	76.6
950				91.5	17.9	85.0	90.8	19.9	88.5	81.7	30.0	87.0

¹ Based on fresh feed.

In the accompanying drawings, Figure 1 is a plot of yield of C_7 isomers vs. percent conversion of the normal C_7 fraction for catalyst A.

Figure 2 is a plot of conversion of normal C_7 fraction vs. reaction temperature in $^{\circ}\text{F}$. for the catalyst of Figure 1.

Figure 3 is a plot similar to Figure 1, but for catalyst B.

Figure 4 is a plot similar to Figure 2, but with the catalyst of Figure 3.

Figure 5 is a plot of percent aromatic yield versus reaction temperature.

Figure 6 is a plot of C_5 and heavier CFRR clear octane number versus volume percent of C_5 and heavier reformed product yield.

The data for Figures 1 to 4 inclusive were taken from Table I of Example I. Referring to the drawings, Figure 1 is a plot of yield of isomerized C_7 hydrocarbons versus conversion of the normal C_7 fraction obtained from the mixture reformed in Example I. The data for the curve (curve P) of this figure is plotted for catalyst A. Curve P is drawn through all of the points, both when diethyl amine was used and when it was not used. The curve (curve S) of Figure 3 is similar to that of Figure 1, but is plotted for catalyst B and represents the curve drawn through all of the points both when using diethyl amine and when not using it.

It will be noted from the curves of these figures that each catalyst exhibits a maximum yield of isomerized hydrocarbon with respect to conversion of the normal C_7 fraction. It will be further noted that the curves are very similar in shape and the maxima occur at approximately the same percent conversion, i. e., 70 percent. For purposes of clarity, a dotted vertical line has been drawn through these maxima and continued into the corresponding conversion vs. reaction temperature curves below. In Figure 1, this dotted line is designated as line 1 and continues into Figure 2. In Figure 3, this line is designated as line 3 and continues into Figure 4. In Figure 1, line 2 is drawn at an angle of 45° from the two co-ordinate axes to represent the line of 100 percent isomerization selectivity, that is, all of the C_7 's converted are converted to C_7 isomers. In Figure 3, line 4 represents the line of 100 percent isomerization selectivity.

It is apparent from Figures 1 and 3 that the point of maximum isomer yield is not only at a high conversion level, but also at a high isomerization selectivity, the selectivity being about 80 percent. This may be calculated from the curve since the ratio of the isomer yield at the maximum to the isomer yield corresponding to the intersection of line 1 and line 2, represents the isomerization selectivity at that conversion. Since the curve is relatively flat on both sides of the maximum, it is also apparent that there is a reasonably wide range of high isomer yields at high isomerization selectivities.

Curve Q of Figure 2 is a plot of the reaction temperature vs. conversion of the normal C_7 fraction of the blend when using catalyst A without the addition of a nitrogen-containing compound, i. e., diethyl amine. Curve R of Figure 2 shows this relationship when 0.1 weight percent nitrogen as diethyl amine is introduced into the reaction zone with the feed. Curves T and W of Figure 4 show the conversion of the normal C_7 fraction vs. reaction temperature relationship for catalyst B without diethyl amine and with 0.03 weight percent nitrogen as diethyl amine, respectively.

Referring again to the drawings, it will be noted in Figure 2 that line 1 representing the percent conversion of normal C_7 's at maximum C_7 isomer yield intersects curve Q (extended) at a temperature of about 690°F . and intersects curve R at a temperature of about 890°F . This means that by the introduction of diethyl amine, the temperature range at which maximum isomer yield is obtained has been raised approximately 200°F . for catalyst A.

Curve N of Figure 5 is a plot of percent aromatic yield vs. reaction temperature for the data of both catalyst A and catalyst B of Table I. It will be seen from curve N that at the low temperatures required for maximum C_7 isomer yield, when no diethyl amine is used with catalyst A there would be no aromatic yield and in fact some of the aromatics present in the feed would probably be lost through hydrogenation. When diethyl amine is used however with catalyst A, the temperature for maximum isomer yield at high isomerization selectivity is raised to about 890°F . which is within the range of the desired high aromatic production as shown by curve N.

Likewise, if the data and curves for catalyst B are examined, it will be seen that the addition of diethyl amine raises the temperature range for maximum isomer yield about 100°F . Referring to curve N of Figure 5, it will be seen that this permits an increase in aromatic yield of from 50 percent up to 80 percent. Obviously, therefore, the use of diethyl amine allows operation in the direction of maximum aromatic yield while retaining maximum isomer yield at high selectivity. Furthermore, another important fact is apparent from these data and curves, namely, since the surface area of the metal oxide base of catalyst B has been lowered from 425 to 155 square meters per gram, this catalyst produces a maximum yield of isomers at high selectivity in a temperature range higher than that of a catalyst whose metal oxide base has not been modified. Consequently, a smaller amount of diethyl amine can be used with catalyst B than with catalyst A to raise the temperature range for maximum isomer yield at high selectivity into the range suitable for maximum aromatic production.

It was stated hereinbefore that the addition of ammonia, or compounds which would produce ammonia under the process conditions, could be used to control the isomerization reaction of catalysts which had unaltered or slightly altered metal oxide bases. The data set forth in Table I and Figures 1 to 5 inclusive, conclusively demonstrate that this may be accomplished.

EXAMPLE II

A commercial silica-alumina cracking catalyst (about 87% silica, 13% alumina) whose surface area had been reduced by steam treatment to 39 square meters per gram was impregnated with about 1.0 percent by weight of platinum. This catalyst was employed for reforming an East Texas reformer stock of 170°F . to 370°F . ASTM boiling range, 56 clear octane number, in a semicommercial unit over an extended period of time until its activity had declined materially. During the run, the reactor temperature had been increased approximately 100°F . to compensate for the gradual decline in activity of the catalyst. The other conditions: pressure—500 p. s. i. g., space velocity—2, hydrogen to hydrocarbon mol ratio—10:1, had been held constant. At this point there was being produced 211 standard cubic feet of gas (mainly, normally gaseous hydrocarbons) per barrel of feed, and 629 standard cubic feet of hydrogen per barrel of feed.

Without changing any of the other conditions, 0.03 weight percent of nitrogen as diethanol amine was introduced with the feed into the system. The gas production dropped to 169 standard cubic feet per barrel of feed and the hydrogen produced rose slightly to 646 standard cubic feet per barrel of feed. After the unit had operated under these conditions for a sufficient time to establish a leveled-out operation, the diethanol amine was removed from the feed and it was found that the gas production again rose to about 210 standard cubic feet per barrel of feed and the hydrogen production to 620 standard cubic feet per barrel of feed. It was noted in this experiment and all subsequent experiments, that the molar hydrocarbon distribution of this gas did not change during the addition of diethanol amine.

Gas production is a measure of isomerization selectivity, that is, a small amount of gas production indicates a high isomerization selectivity, and conversely a large amount of gas production indicates a low or poor isomerization selectivity. Thus, when the gas production dropped as in the above experiment, the isomerization selectivity increased. Hydrogen production, however, is directly related to aromatic production, that is, a high hydrogen production indicates a high yield of aromatics from the dehydrogenation reaction and a low yield of hydrogen indicates a poor yield of aromatics.

These runs demonstrate that the isomerization selectivity of a partially spent platinized acidic metal oxide reforming catalyst may be raised to a high level and the balance among the reactions restored by the addition of small amounts of a compound which can be converted to ammonia under the process conditions. This unit was operated with hydrogen recycle so that some of the ammonia produced from the conversion of the diethanol amine was recycled with the hydrogen. Analysis indicated that the ammonia recycled (calculated as nitrogen) amounted, at a leveled-out condition, to about five times the amount of diethanol amine (nitrogen basis) introduced with the fresh feed, therefore, there was a total of 0.18 percent by weight of nitrogen in the vapors and gases passing over the catalyst. These data also show that when the introduction of diethanol amine was stopped the operation returned to the same level as before the introduction of the diethanol amine, indicating that the presence of nitrogen has no permanent effect on the catalyst.

EXAMPLE III

A silica-alumina cracking catalyst whose surface area had been reduced by steam treatment to about 85 square meters per gram was impregnated with about 0.45 percent by weight of platinum. This catalyst was employed for reforming the same East Texas reforming stock of Example II in the same unit as Example II at 500 p. s. i. g., space velocity of 3, hydrogen to hydrocarbon mol ratio of 10:1 at several temperatures to establish points for a yield-octane relationship.

Table II which follows sets forth the variables and the results obtained.

Table II

	Gas prod. std. cu. ft. per barrel of feed	H ₂ prod. std. cu. ft. per barrel of feed	Yield of C ₆ and heavier gasoline vol. per- cent based on feed	CFRR octane, clear, C ₆ and heav- ier basis
Without ammonium hydroxide:				
Run 1.....	205	645	87.5	81.1
Run 2.....	168	463	89.1	78.9
With 0.01% nitrogen as ammonium hy- droxide:				
Run 3.....	195	871	85.4	87.0
Run 4.....	83	645	92.0	77.0
Run 5.....	63	546	94.1	72.6

The yield-octane data from the above Table II are plotted in Figure 6. Curve X represents the yield-octane relationship obtained with this catalyst when no ammonium hydroxide was introduced into the system. Curve Y represents the yield-octane relationship obtained when 0.01 percent of nitrogen as ammonium hydroxide was introduced into the system. A comparison of these curves shows that although the surface areas of the silica-alumina base had been altered to a considerable extent, the reforming reactions were not in the most optimum ratios of one to another, but that by the addition of a small amount of ammonia it was possible to bring the ratios to the optimum point with a markedly improved yield-octane relationship. It is to be noted that in the example under the hydrogen recycle and other operating conditions, the actual concentration (based on feed) of

nitrogen as ammonia in contact with the catalyst is six times the figure given for the percent introduced with the feed.

EXAMPLE IV

A catalyst similar to that in Example III was employed for reforming the same East Texas reformer stock of Examples II and III and under the conditions of Example III, with certain variations.

In this example nitrogen concentration effects at constant reaction temperature and reaction temperature effects at constant nitrogen addition were determined. The results of these experiments are set forth in Table III which follows:

Table III

Reaction temperature in ° F.	Weight percent nitrogen as NH ₄ OH in feed	Gas, std. cu. ft. per barrel of feed	H ₂ produc- tion, std. cu. ft. per barrel of feed
920.....	0.017	126	701
920.....	0.03	90	709
920.....	0.06	79	711
880.....	0.06	58	693
900.....	0.06	63	736
920.....	0.06	80	789
950.....	0.06	101	835

It will be seen from these data that as the concentration of nitrogen in the form of ammonium hydroxide over the catalyst is increased, the gas production decreases, however, the effect diminishes with increasing concentration. The data at constant nitrogen addition show that by combining temperature and concentration, it is possible to operate at the most optimum reforming conditions. As in Example III, the actual concentration of nitrogen over the catalyst is six times that given because of the recycle effect.

The foregoing examples have demonstrated the novel and unusual method of controlling reforming processes by the addition of ammonia, or compounds which will yield ammonia under the reforming process conditions. This control is based upon the novel discovery that maximum yield of isomers with a high isomerization selectivity can be produced in a range of maximum aromatic formation with platinized acidic metal oxide type catalysts when employing the addition of ammonia or its equivalents to the reaction system.

In the foregoing examples various specific operating conditions for the reforming reaction were employed. In general, temperatures in the range of 600 to 1000° F., pressures from 100 to 1000 p. s. i., liquid hourly velocities in the range of 0.1 to 10, and hydrogen in amounts ranging from 1 to 20 mols of hydrogen per mol of hydrocarbon may be used. These ranges however should not be construed as limiting, but are merely illustrative of general reforming conditions within which applicants' invention is particularly applicable. Furthermore, the invention is equally applicable to reforming processes employing acidic metal oxide bases impregnated with palladium as the catalyst. The amounts of the various components of the catalysts may be varied in accordance with the known art describing catalysts of this type. For example, the amount of platinum or palladium which is impregnated on the acidic metal oxide may range preferably between 0.1 percent and 2.5 percent by weight of the final catalyst.

The hydrocarbon fractions which may be charged to reforming processes operated in accordance with the teachings of this invention include: petroleum distillates such as naphthas, gasoline, kerosene, and higher boiling fractions, and similar fractions from other sources such as from the Fischer-Tropsch process, but in particular straight run and thermally cracked or reformed fractions boiling in the gasoline range or combinations of such fractions.

We claim:

1. In a process for catalytically reforming a hydrocarbon fraction boiling within the gasoline-kerosine range to increase the anti-knock value thereof in the presence of hydrogen and a catalyst comprising an acidic metal oxide component impregnated with a metal from the group consisting of platinum and palladium in which the reaction temperature for maximum isomer production at high selectivity is of less severity than is the reaction temperature for the maximum production of aromatics, the step of increasing the reaction temperature for maximum isomer production at high selectivity in the direction of the severity of the reaction temperature for producing maximum aromatics which comprises conducting the reforming process in the presence of at least one nitrogen-containing compound from the group consisting of ammonia and compounds which will yield ammonia under the reforming process conditions without the deposition of a solid residue on the catalyst in an amount sufficient to permit an increase in the reaction temperature applicable to maximum isomer production at the desired selectivity and increasing the reaction temperature within the range of the reaction temperature for the maximum production of aromatics, thereby to produce simultaneously maximum aromatics and maximum isomers at the desired selectivity.

2. The process according to claim 1 in which the amount of the nitrogen-containing compound ranges between 0.005 percent and 3.0 percent by weight of nitrogen based upon the weight of the hydrocarbon charge.

3. The process according to claim 1 in which the acidic metal oxide component of the catalyst is silica and alumina and the metal which is used to impregnate the acidic metal oxide component is platinum.

4. The process according to claim 1 in which the acidic metal oxide component of the catalyst is silica and zirconia and the metal which is used to impregnate the acidic metal oxide component is platinum.

5. The process according to claim 1 in which the acidic metal oxide component of the catalyst is silica, alumina, and zirconia, and the metal which is used to impregnate the acidic metal oxide component is platinum.

6. The process according to claim 1 in which the acidic metal oxide component of the catalyst is silica and magnesia and the metal which is used to impregnate the acidic metal oxide component is platinum.

7. The process according to claim 1 in which the acidic metal oxide component of the catalyst is silica, alumina, and magnesia, and the metal which is used to

impregnate the acidic metal oxide component is platinum.

8. In a process for catalytically reforming a hydrocarbon fraction boiling within the gasoline-kerosine range to increase the anti-knock value thereof in the presence of hydrogen and a catalyst comprising silica and alumina impregnated with platinum in which the reaction temperature for maximum isomer production at high selectivity is of less severity than is the reaction temperature for the maximum production of aromatics, the step of increasing the reaction temperature for maximum isomer production at high selectivity in the direction of the severity of the reaction temperature for producing maximum aromatics which comprises conducting the reforming process in the presence of at least one nitrogen-containing compound from the group consisting of ammonia and compounds which will yield ammonia under the reforming process conditions without the deposition of a solid residue on the catalyst in an amount ranging between 0.005 percent and 3.0 percent by weight of nitrogen based upon the weight of the hydrocarbon charge to permit an increase in the reaction temperature applicable to maximum isomer production at the desired selectivity and increasing the reaction temperature within the range of the reaction temperature for the maximum production of aromatics, thereby to produce simultaneously maximum aromatics and maximum isomers at the desired selectivity.

9. The process according to claim 8 in which the nitrogen-containing compound is ammonia.

10. The process according to claim 8 in which the nitrogen-containing compound is ammonium hydroxide.

11. The process according to claim 8 in which the nitrogen-containing compound is diethyl amine.

12. The process according to claim 8 in which the nitrogen-containing compound is diethanol amine.

13. The process according to claim 8 in which the nitrogen-containing compound is aniline.

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