Oct. 18, 1960 R. FLEMING ET AL 2,956,945

REFORMING GASOLINE RANGE HYDROCARBONS IN THE PRESENCE OF AMMONIA

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Fig. 1

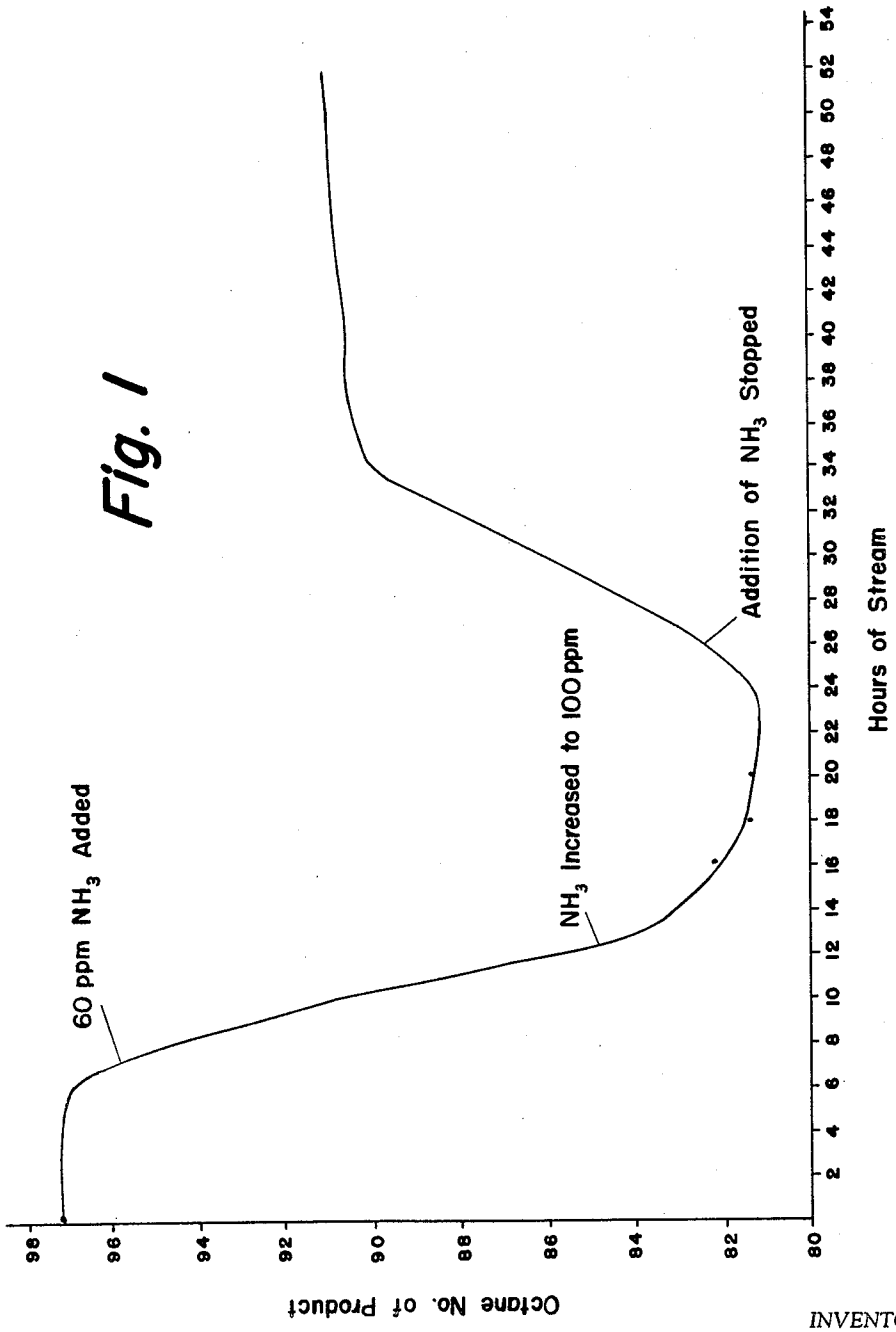

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Fig. 2

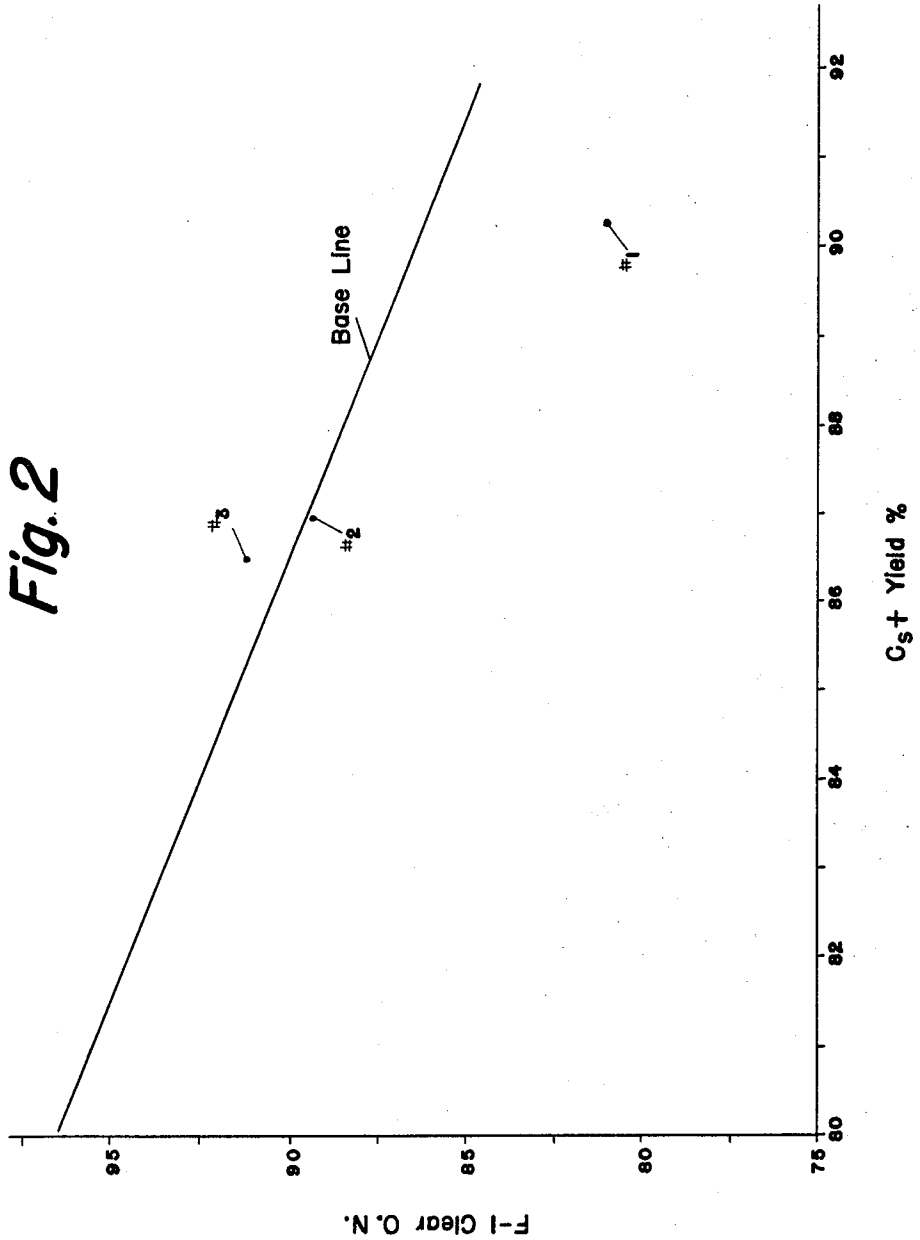

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Fig. 3

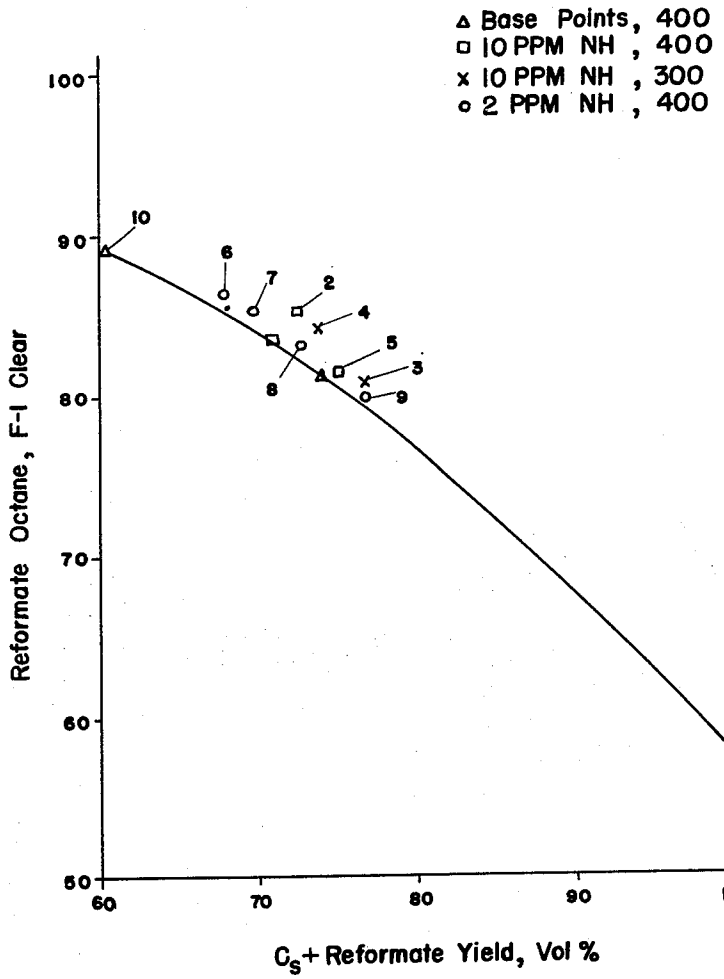

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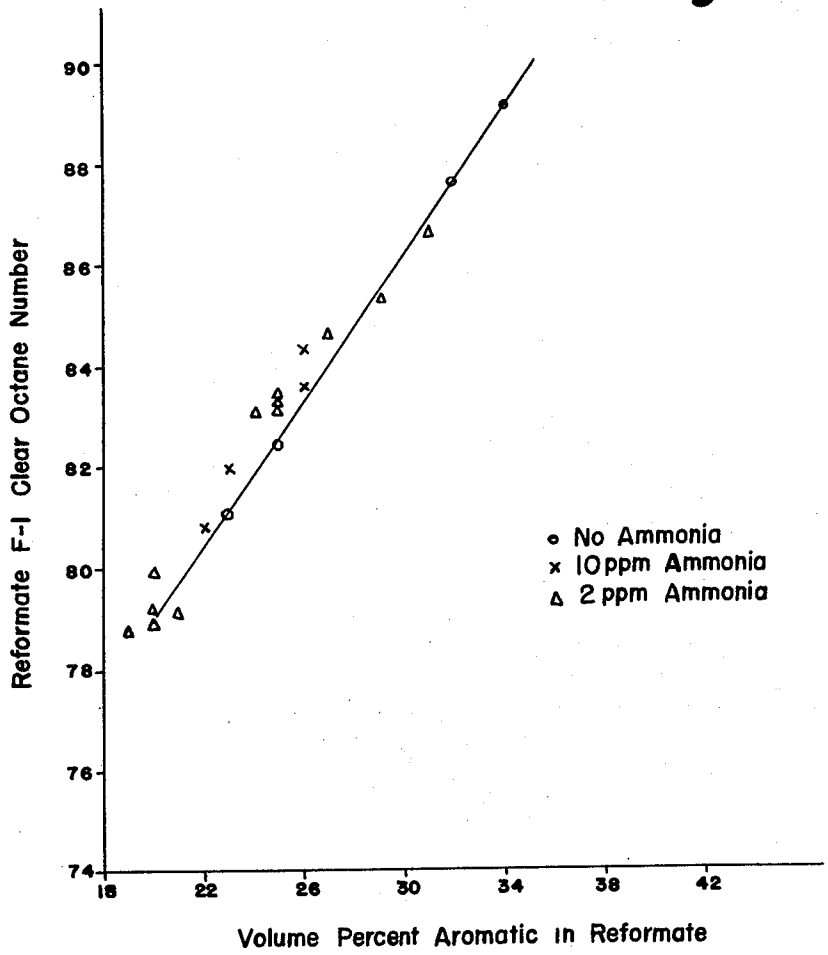
Fig. 4



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REFORMING GASOLINE RANGE HYDROCARBONS IN THE PRESENCE OF AMMONIA

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1 Claim. (Cl. 208—65)

This invention relates to a process for catalytically reforming hydrocarbons boiling in the gasoline boiling range to yield high-octane gasoline blending stocks, and more particularly to a process for reforming feed stocks low in naphthenic components.

Commercial processes for the catalytic reforming of straight run gasoline fractions are commonly operated either to produce a high octane fraction for use as a gasoline blending component, or to produce petrochemicals such as benzene, toluene, or xylene. When high octane gasoline is the desired product, the feed to the process may be a full boiling range, straight run gasoline, but preferably is a higher boiling fraction of the gasoline, such as a 260–375° F. fraction. If petrochemicals are desired, narrow-cut fractions are used as a feed, such as a 150–194° F. cut for benzene production, a 215–240° F. cut for toluene production, and a 240–265° F. cut for xylene production. Whether or not the process is operated for gasoline or petrochemical production, the reactions taking place are essentially the same, involving dehydrogenation of naphthenes to the corresponding aromatics, dehydrocyclization of paraffins, isomerization and hydrocracking. Of these reactions, dehydrogenation and dehydrocyclization are strongly endothermic, while the other reactions are either exothermic or substantially thermally neutral.

The rate of dehydrogenation is faster than the other reactions, so that, in reforming processes using fixed beds of catalyst, there is an initial rapid drop in temperature as the feed passes through the catalyst. In order to compensate for this temperature drop, it is the practice to divide the catalyst into a number of parts, and to pass the feed through a series of catalyst cases, while reheating the feed to reaction temperature between catalyst cases. Thus, in a three-case commercial reactor processing a 260–375° F. straight run gasoline, the feed, preheated to 950° F., is passed through the first case in which the principal reaction is dehydrogenation of naphthenes, with an accompanying drop in temperature of about 65° F. to about 100° F., depending on the naphthene content of the feed. The effluent from the first case is then reheated to 950° F. and is passed to the second catalyst case, in which further dehydrogenation of naphthenes is accomplished, together with dehydrocyclization, hydrocracking, and isomerization. Since the major portion of the naphthenes were dehydrogenated in the first catalyst case, the temperature drop in the second case is lower than in the first, about 20° to 35° F. The effluent from the second case is then reheated and passed to the last catalyst case, in which the principal reactions involve low octane number, straight chain paraffins which are hydrocracked and dehydrocyclized to higher octane aromatics and paraffins. Since the feed to the last catalyst case is substantially free of naphthenes, there is little or no drop in temperature.

A typical reformate recovered from an operation of this type will boil between 175° F. (5% over) and 375° F. (95% over) and will have an octane number of 89

(F–1 clear). It will comprise about 52% aromatics, 2% olefins, 2% naphthenes, and 44% paraffins, which latter have an octane number of only about 58. It is clear that if anything can be done to improve the octane number of these paraffins, then at the same yield of reformate, the octane number of the total gasoline would be increased, or, in the event that a gasoline of the same octane number is to be obtained, the process could be run under milder conditions to produce a less aromatic gasoline, with consequent increase in yield of liquid product. A gasoline having a lower aromatic content also has the advantage that it has a higher lead susceptibility, since only the paraffinic constituents of a gasoline are increased in octane number by the addition of lead teteraethyl. For example, a straight paraffinic gasoline may have its octane rating increased by 14 numbers by addition of 1.5 ml. of tetraethyl lead per gallon, whereas a gasoline containing 40% aromatics will be improved by only 8 numbers by the addition of the same amount of lead, and a gasoline containing 60% aromatics will be improved by only 5 numbers.

In the event that the reforming process is operated to produce pure aromatics for sale as petrochemicals, conditions of operation are adjusted so that the last of the naphthenes are dehydrogenated in the final catalyst case. The reformate is then solvent extracted to recover pure aromatics and a low octane paraffinic raffinate. A typical raffinate from a reforming process operated to produce benzene and toluene has a boiling range of from 168° F. (5% over) to 212° F. (95% over), has a composition of 3% olefins, 5% aromatics, 3% naphthenes, and 89% paraffins, and has an octane number of about 60, too low to make it valuable as a gasoline blending stock. The raffinate may be upgraded by re-reforming under severe conditions, but losses to normally gaseous hydrocarbons are high, and the liquid yield, when reforming to an 85 O.N. product, is only about 68% of the charge. As in the case of full gasoline boiling range reformate, the product contains a considerable quantity of low-octane hydrocarbons, chiefly n-hexane and n-heptane, and any conversion of these paraffins to higher octane products, over and above that produced by conventional reforming, would be exceedingly attractive from an economic standpoint.

It is an object of this invention to provide a process for reforming hydrocarbons in the gasoline boiling range which produces a higher octane number product at a given yield than is obtainable by a conventional reforming process.

It is a further object of this invention to provide a process for reforming hydrocarbons in the gasoline boiling range which produces a less aromatic product at a given octane number than is obtainable by a conventional reforming process.

We have now discovered that the foregoing objects may be attained by adding a small amount of ammonia or a nitrogen compound convertible to ammonia under reforming conditions such as an amine, which decomposes to yield ammonia, in the range of 2 to 100 parts per million, to a gasoline boiling range hydrocarbon fraction substantially free of naphthenes, prior to reforming the fraction in the presence of a platinum catalyst. By the term "substantially free of naphthenes" we do not mean that no naphthenes at all are present. We use the term to describe a fraction which contains only a small percentage of naphthenes, 10% or less by volume. If the ammonia is added to a petroleum fraction containing more than about 10% naphthenes, and the fraction is then reformed, the yield/octane relationship is unfavorably affected, whereas the opposite is true if the fraction contains less than about 10% naphthenes. The favorable effect of small amounts of ammonia in

reforming low-naphthene feed stocks is surprising, since the prior art indicates that larger amounts of ammonia poison the ability of platinum catalysts to promote hydrocracking, isomerization, an dehydrocyclization. Contrary to what is suggested by the prior art, we have found that ammonia, in amounts less than 100 p.p.m., promotes isomerization, since only by extensive isomerization of paraffins to more highly branched structures can a gasoline be produced which, for a given octane number, contains less aromatics than a gasoline produced by reforming in the absence of ammonia.

If the present invention is to be utilized in a reforming process for the production of high octane gasoline from a straight run gasoline fraction in a multicase reformer, the ammonia should be added just prior to the last catalyst case, since the effluent from the next to last case will be essentially free of naphthenes. If added earlier in the process, when a large proportion of the naphthenes in the feed remain unconverted, the ammonia will have an adverse effect on the yield-octane relationship. When the invention is to be employed in up-grading a paraffinic by-product fraction derived from a process for the production of aromatics from petroleum fractions, the ammonia may be added to the feed prior to its introduction to the reformer, since such paraffinic fractions are substantially free of naphthenes.

The discovery leading to the present invention was made in the course of a run made to determine the effect of ammonia on a platinum reforming catalyst. The catalyst contained 0.6% platinum supported on alumina containing about 0.6% combined chlorine. The run was made in a three case reactor, with reheating between the catalyst cases to maintain the inlet temperature to each reactor at about 950° F. The feed was a straight run gasoline fraction boiling from 260° F. to 375° F., pressure was 400 p.s.i.g., hydrogen/hydrocarbon ratio 5 to 1, and the liquid hourly space velocity was 3.5. Data obtained during this run are plotted in Figs. 1 and 2 of the accompanying drawings, Fig. 1 showing the octane number of the reformate as the run progressed, while Fig. 2 shows the yield-octane relationship of the products at three points during the run, compared to a standard yield-octane base line obtained by reforming the same feed stock at various severities in the absence of ammonia. As will be noted from Fig. 1, for the first six hours of the run the octane number of the product held constant at about 97. Beginning at the end of the sixth hour, 60 p.p.m. of ammonia, based on the feed, was continuously added thereto. At the end of 14 hours of operation, the octane number of the product had dropped to 83. Ammonia was then increased to 100 p.p.m., and the operation was continued for another ten hours. During the last six hours of this portion of the run, the octane number held fairly constant at about 81, and the yield of C_5+ product was 90.7% of the charge (point #1 on Fig. 2). As may be observed, the yield-octane relationship was very poor compared to operation without ammonia, since at this yield a product having an octane number of about 86.5 would be expected in normal operations.

After 24 hours addition of ammonia was stopped, but the run was continued to determine whether the ammonia had permanently deactivated the catalyst, or whether it was merely a temporary poison, which could be desorbed from the catalyst to restore it to its former activity and selectivity. It will be noted from Fig. 1 that the octane number of the reformate rose rapidly during the 24–34 hour period. At the end of 34 hours, the octane number of the product had risen to 90, indicating that ammonia had been desorbed from a considerable amount of the catalyst, but that some adsorbed ammonia still remained, probably only in the second and third catalyst cases. At the end of 33 hours, the octane number of the product had risen to 89, at a yield of C_5+ product of 87% (point #2 on Fig. 2), a yield-octane relationship essentially that which would be obtained if no ammonia had been used. During the remaining 18 hours of the run, the octane number of the product rose gradually to 91.5. At the end of the run, however, the yield at this octane number was 86.6 (point #3 on Fig. 2), more than 1% greater than would be expected at this octane number. Stated another way, the octane number was more than 1 number higher than would be expected at equal yield if no ammonia had been used. This surprising result could only be explained by the theory that some ammonia still remained adsorbed on the catalyst in the third case, where it was acting as a promoter to increase the selectivity of the catalyst. It was thus apparent that in the first two catalyst cases, in which naphthenes formed a large proportion of the feed, the ammonia poisoned the selectivity of the catalyst, whereas in that portion of the apparatus in which little or no naphthenes were present, the action of the ammonia was reversed.

In order to test the correctness of this theory, a number of runs were made using as a feed stock a low-naphthene paraffinic raffinate obtained from a solvent extraction process for separating benzene and toluene from a light reformate. This feed had a boiling range of from about 150° F. to about 220° F., had an octane number of 57.5, and contained about 3% naphthenes, the balance being chiefly C_6 and C_7 paraffins. Hydrogen to hydrocarbon molar ratio was in all cases 5:1, and liquid hourly space velocity was 2.4; but temperature was varied from 915° F. to 940° F., and pressure was varied from 300 to 400 p.s.i. in order to determine what yields could be obtained at various octane number levels. One series of runs was made with 10 p.p.m. ammonia in the feed; another series was made with only 2 p.p.m. ammonia in the feed. Data from these runs are plotted on Figs. 3 and 4 of the accompanying drawings, along with data obtained from other runs with the same feed stock but without ammonia. The same catalyst was used as was used in the run plotted in Fig. 1.

Referring more particularly to Fig. 3, it will be noted that the yield-octane relationship of the runs using ammonia in the feed was consistently better than in the runs without ammonia. This is particularly evident in points 2 and 4. The run from which the data of point 2 was derived was at 930° F. and 400 p.s.i.g., with 10 p.p.m. ammonia. It will be noted that the 72.5% yield at 85.2 octane number was 4% greater than that obtainable at the same octane number without ammonia. A run under similar conditions without ammonia gave a product having an 89 octane number in 60% yield (point #10 on Fig. 3). Thus, while the addition of ammonia caused a drop of 3.8 octane number, the yield was increased by 12.5% based on feed, or 21% based on the reformate produced at 930° F. without ammonia. Even 2 p.p.m. of ammonia significantly improved the yield-octane relationship of the reformate, as indicated by points 6, 7, 8 and 9 on Fig. 3, all of which lie above the yield-octane curve obtained without ammonia.

Referring now to Fig. 4, it will be observed that when ammonia is added to the feed, for a given octane number, the reformate is less aromatic than that produced without ammonia, indicating that the ammonia promotes isomerization of paraffins to more highly branched, higher octane paraffins. The data plotted in Fig. 4 was obtained using the paraffinic raffinate described above as a feed stock. Such low-aromatic products have a greater lead susceptibility than products having a higher aromatic content, and therefore require less tetraethyl lead per gallon to raise their octane number to a given value. In addition, they are cleaner-burning in an internal combustion engine, and cause less engine deposits.

While the increase in yield of reformate for a given octane number produced by the addition of ammonia to a low-naphthene feed may appear to be small percentage-wise, it is of real economic significance. Thus, if addition of ammonia prior to the last catalyst case of a reformer charging 30,000 barrels a day of straight run

gasoline increases recovery of C_5+ hydrocarbons by 1%, the plant will produce 300 barrels, or 12,600 gallons more than it will produce without ammonia. At the present price of about 11.5 cents per gallon for 92 octane gasoline, the value of the products will be increased by about $1400 per day, or approximately $500,000 per year.

The invention claimed is:

In a process for reforming petroleum fractions in which a petroleum feed stock boiling in the gasoline boiling range is passed through a series of catalyst cases containing a platinum supported on a halogen-containing alumina reforming catalyst, in the presence of added hydrogen and under reforming conditions of temperature and pressure with reheating to reaction temperature between the cases, the improvement which comprises adding to the effluent from the next to last case of the series an amount of a compound selected from the group consisting of ammonia and amines, sufficient to yield from about 2 to about 100 parts per million of ammonia in the reaction mixture contacting the effluent together with such added compound with a platinum reforming catalyst in the last catalyst case of the series of reforming conditions of temperature and pressure, and recovering a liquid product having a higher octane number than the feed stock.

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