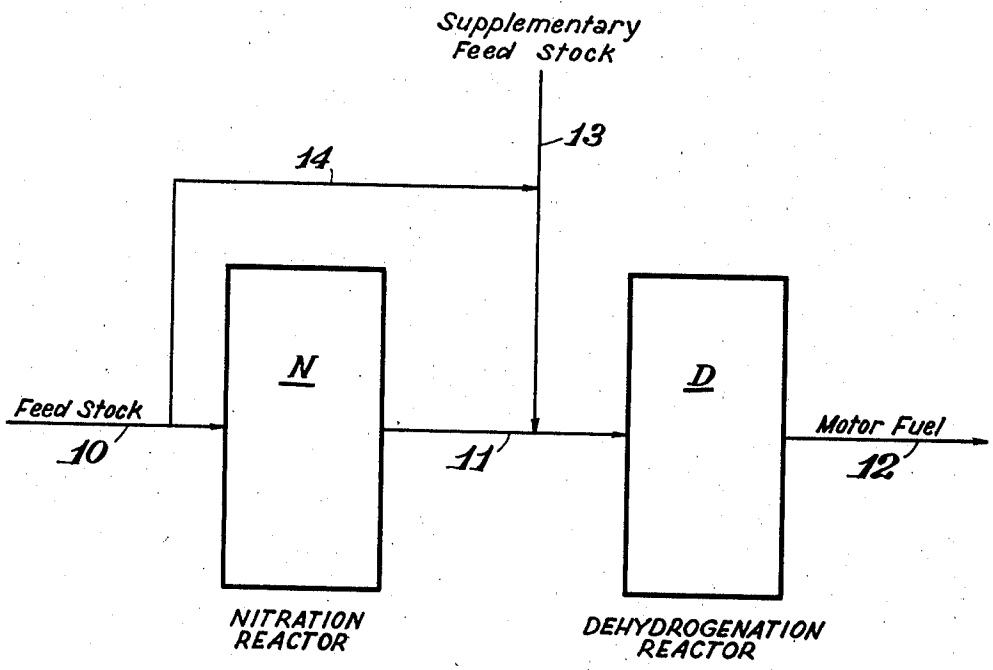
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GASOLINE MANUFACTURE

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GASOLINE MANUFACTURE

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This invention relates to an improved process for the production of motor fuels characterized by high octane numbers. More particularly it relates to an improved process for the production of high octane number gasoline by the simultaneous reduction of nitro hydrocarbons to amines and the dehydrogenation of low octane number naphthas.

It is an object of our invention to provide an improved process for the production of high antiknock gasoline containing organic amines. Another object is to provide a process whereby at least a portion of the hydrocarbon feed to a dehydrogenation process is nitrated, and the nitrated portion converted to hydrocarbon amines in the dehydrogenation process.

A still further object of our invention is to provide a process wherein the hydrogen from the dehydrogenation of hydrocarbons is utilized in situ for the reduction of nitro organic compounds to organic amines, the hydrogen removal serving to permit the formation of an additional amount of olefins in the dehydrogenation process.

In brief, we contemplate the partial nitration of at least a portion of the feed stock to a dehydrogenation process, the feed stock being low antiknock naphtha containing aromatics, and the nitrated product being directed to the dehydrogenation process wherein the hydrogen derived therefrom serves to reduce the organic nitro compounds to organic amines at the same time that the remainder of the feed stock is being converted to motor fuel of high antiknock properties.

The accompanying drawing which forms a part of this specification illustrates diagrammatically one method of carrying out our invention.

A feed stock comprising hydrocarbons boiling within the gasoline boiling range enters through line 10. This feed stock is preferably a naphtha boiling from about 90° F. to about 400° F. and while it may be obtained from any suitable source we prefer to use a naphtha from the distillation of crude oils. These naphthas, known as "straight-run" or "virgin" naphthas, are characterized by low octane numbers and therefore are not desirable for use in the modern automobile engine, since these engines have been designed to use gasolines of much higher antiknock characteristics. These naphthas are made up essentially of paraffinic hydrocarbons with a small amount of aromatic hydrocarbons and naphthenic hydrocarbons present. The aromatic content is generally not more than 20% by volume, and usually not more than about 15% by volume.

We propose to convert at least a part of the aromatics found in such a stock to nitro-aromatics. This can be carried out in a number of different ways and the nitration process is indicated in the drawing as N. It should be understood that in the drawing this represents an integrated process so that the nitrated hydrocarbons which pass from nitration reactor N through line 11 to dehydrogenation reactor D are free of nitrating agent and any undesirable products which may have been formed during the nitration.

The nitration can be carried out in any one of a number of different ways. We can use for example, a mixture of concentrated sulfuric acid and concentrated nitric acid, the temperature being maintained at from —20° to 100° F. in order to avoid the formation of the dinitro compounds have have been found much less satisfactory for our purpose than the mononitro hydrocarbons.

Nitration can also be carried out according to the method of Hopkins in U. S. Patent 1,558,027 in which aluminum nitrate and nitric acid act as the nitrating agents, the reaction being carried out at approximately 265° to about 300° F.

The nitration of petroleum naphthas can also be carried out in the vapor phase with nitric acid according to the method of Haas et al. as described in U. S. Patent 1,967,667 and U. S. Patent 2,071,122 as well as in Industrial and Engineering Chemistry 28, 399 (1936). Nitration can also be accomplished by the use of fuming nitric acid, care being taken to regulate the temperature from about —20° F. to about 75° F. so that the formation of the dinitro compounds does not occur to any great extent.

The product from the nitration, as has been pointed out, will be chiefly nitro aromatics since these will nitrate in preference to the paraffins present. However, there may be some conversion of the aliphatic hydrocarbons to nitro-aliphatics. The nitrated hydrocarbons are directed through line 11 to dehydrogenation reactor D wherein the unnitrated hydrocarbons are dehydrogenated and the nitrated hydrocarbons are reduced to organic amines.

Dehydrogenation in reactor D is preferably carried out by catalytic means. Dehydrogenation reactor D represents an integrated dehydrogenation process with heating means, fractionating means, pumps, etc. and the proper apparatus is well known to one skilled in the art.

Although there are many catalysts available for this purpose we prefer to use such catalysts as chromium oxide gels, mixed aluminum oxide-chromium oxide, mixed molybdenum oxide-alumina, magnesium chromite or other chromium or molybdenum-containing catalysts since these have been found to be effective in the reduction of nitro hydrocarbons with simultaneous dehydrogenation of unnitrated hydrocarbons.

The dehydrogenation reaction is carried out at from about 850° F. to about 1100° F. and preferably at about 950° F. and under pressures of from 0.5 atmosphere to about 5 atmospheres and preferably at about atmospheric pressure or slightly above. The reaction is carried out at a space velocity of from about 0.1 to about 5.0, and preferably at a space velocity from about 0.5 to about 0.6; i. e. there should be from about 0.1 to about 5.0 liquid volumes of hydrocarbon feed per volume of catalyst space per hour, and preferably from about 0.5 to about 0.6 liquid volumes of naphtha per volume of catalyst space per hour.

The product from reactor D is withdrawn and sent to storage through line 12. This product will comprise unconverted naphtha, organic amines, aromatic and olefinic hydrocarbons. By employing the conditions set forth above, we obtain only a comparatively small amount of aromatic hydrocarbons by the dehydrogenation of paraffins, or to some extent, the naphthenes present. Under other conditions, particularly lower space velocity, the dehydrogenated olefins are converted to aromatic hydrocarbons in considerable amounts. By producing chiefly olefins, however, a higher volume yield can be obtained, and also a product having a "high blending value," i. e. a product which, when blended with a low antiknock gasoline, will increase the octane number of that gasoline to a greater extent than will blending an aromatic hydrocarbon of equal volume. For these reasons we prefer to operate in such a manner that the olefin content of the naphtha is increased to the greatest practical extent.

In the event that the feed stock contains a substantial amount of aromatic hydrocarbons or a nitration reaction is employed which converts aliphatic as well as aromatic compounds to nitro-compounds, it is advisable to direct a part of the feed stock directly to reactor D through line 14, and direct only so much of the feed stock as will yield the desired amount of organic amines in reactor D through nitration reactor N and line 11. In this way, octane number increase can be obtained without subjecting the entire feed stock to nitration conditions.

Although organic amines may be added to naphthas in amounts limited only by their solubility, and still be effective for increasing the antiknock properties, it has been found that adding more than 8 to 10% does not increase the octane number to the same extent that adding less than 8 to 10% does since above this percentage the octane number is no longer a linear function of the amine percentage. However, within the limits of solubility of the amines in the hydrocarbon product there is no mixture of these to which an addition of the organic amine is completely ineffective to increase the existing octane number.

For the above reason it becomes uneconomical to include in a motor fuel more organic amines than can be successfully utilized in increasing the octane number a number of units for each volume percent of organic amines. Accordingly, in our process, we find it desirable to nitrate only that amount of the feed stock which can be most economically utilized in the motor fuel after reduction. This amount will depend to a large extent on the aromatic content of the feed stock and the effectiveness of the nitration process. For example, if the naphtha contains approximately 20% aromatic hydrocarbons, then about 40 to 60% of the stock should be subjected to nitration while the remainder of the stock is bypassed by line 14 around the nitration reactor N and joins the nitrated stock in the line 11 prior to reactor D through line 13.

If, on the other hand, the feed stock contains only approximately 10 to 15% aromatics, then all of it will enter reactor N through line 10, and line 14 will not be used. If there is more than one feed stock varying in aromatic content, it may be desirable to subject all of the feed stock high in aromatic hydrocarbons to nitration, and add the feed stock low in aromatic hydrocarbons through line 13 to the nitrated hydrocarbons in line 11 in the proper proportion to obtain the desired content of organic amine in the final motor fuel.

It will be seen that we have provided a process in which it is possible to obtain a valuable gasoline characterized by very high octane number. Under the conditions of dehydrogenation described, straight-run naphtha can be converted to a gasoline having 90 octane number while by nitrating the feed stock and directing this to the dehydrogenation reactor, octane numbers above 100 can be attained. Also, by converting the nitro compounds to organic amines under dehydrogenation conditions we can utilize the liberated hydrogen from the dehydrogenated hydrocarbons and employ only a single step for this improvement in octane number, and at the same time obtain an increased yield of dehydrogenated products due to the removal of the hydrogen from the process.

We claim:

1. A process for the production of high antiknock motor fuels from a low antiknock gasoline which comprises incorporating at least one nitroaromatic hydrocarbon in said low antiknock gasoline in an amount sufficient to yield a quantity of aromatic amine which will substantially increase the knock rating of said gasoline and then simultaneously catalytically dehydrogenating said low antiknock gasoline and converting said nitroaromatic hydrocarbon to an aromatic amine.

2. A process for the production of high antiknock fuel from low antiknock hydrocarbon fuels containing at least a minor amount of aromatic hydrocarbons which comprises nitrating at least a portion of said low antiknock fuel to form an amount of nitroaromatic hydrocarbon sufficient to yield a quantity of organic amine which will substantially increase the knock rating of said low antiknock hydrocarbon fuel and subjecting the product from said nitration to catalytic dehydration whereby aromatic amines are formed.

3. A process for the production of a high antiknock motor fuel from low antiknock hydrocarbon motor fuels containing at least a minor amount of aromatic hydrocarbon which comprises nitrating at least a portion of said low antiknock hydrocarbon motor fuels to form nitroaromatic hydrocarbons in an amount sufficient to yield a quantity of aromatic amines which will substantially increase the knock rating of said low antiknock hydrocarbon fuel, cata-

lytically dehydrogenating at least a portion of said low antiknock motor fuel and subjecting said nitroaromatic hydrocarbons to said catalytic dehydrogenation whereby aromatic amines are formed.

4. In a process for the production of a high antiknock fuel from low antiknock hydrocarbon fuels containing at least a minor amount of aromatic hydrocarbons, the steps comprising nitrating at least a portion of said low antiknock hydrocarbon fuel to yield a substantial amount of nitroaromatic hydrocarbons, converting said nitrated low antiknock fuels in a catalytic dehydrogenation process to aromatic amines in an amount sufficient to increase substantially the knock rating of said low antiknock hydrocarbon fuel, and simultaneously dehydrogenating said unnitrated low antiknock fuels.

5. A process for the production of a high antiknock fuel from a low antiknock hydrocarbon fuel containing a substantial amount of aromatic hydrocarbons which comprises nitrating at least a portion of said aromatic hydrocarbons to form nitroaromatics, and subjecting the product from said nitration to catalytic dehydrogenation whereby aromatic amines are formed in an amount sufficient to increase substantially the knock rating of said low antiknock hydrocarbon fuel.

6. A process for the production of a high antiknock fuel from a low antiknock hydrocarbon fuel containing a substantial amount, but less than 20% by volume, of aromatic hydrocarbons which comprises nitrating at least a portion of said aromatic hydrocarbons to form nitroaromatics in a quantity sufficient to yield aromatic amines which will substantially increase the knock rating of said low antiknock hydrocarbon fuel, converting said nitroaromatics in a catalytic dehydrogenation process to aromatic amines and simultaneously dehydrogenating said unnitrated low antiknock hydrocarbon fuel.

7. A process for the production of a high antiknock fuel from a low antiknock hydrocarbon fuel containing from about 10 to about 15% of aromatic hydrocarbons which comprises nitrating said low antiknock hydrocarbon fuel to convert said aromatic hydrocarbons into nitroaromatics, converting said nitroaromatics in a catalytic dehydrogenation process to aromatic amines and simultaneously dehydrogenating the low antiknock hydrocarbon fuel.

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