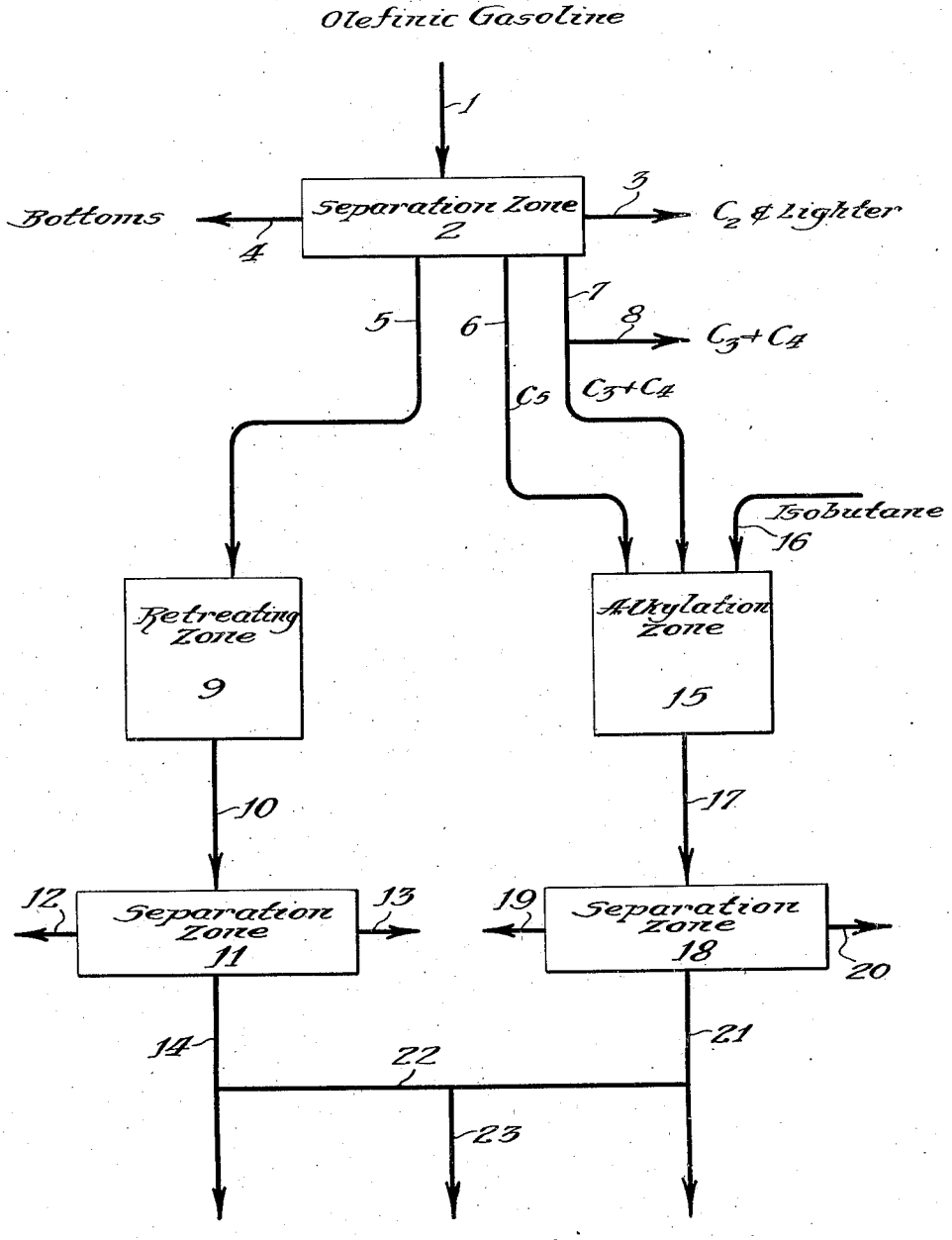
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PRODUCTION OF AVIATION GASOLINE

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PRODUCTION OF AVIATION GASOLINE

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This invention relates to a method for preparing aviation gasoline blending stock from an olefinic gasoline. More specifically, it is concerned with an operation for the conversion of an olefinic gasoline having a low lead response to a less olefinic gasoline having a high lead response and being suitable as an aviation fuel blending stock by reprocessing and alkylation.

Although olefinic gasolines produced by cracking or reforming operations, particularly catalytic cracking or reforming, have high initial octane numbers, they are generally unsuitable as aviation fuel blending stocks because of their high olefin content and low lead susceptibility. It has been necessary, therefore to develop process for "retreating" or "reprocessing" these olefinic gasolines to reduce their olefin content in order to make them suitable for use in aviation fuel. Usually, this "retreating" or "reprocessing" operation is conducted by contacting the olefinic gasoline charging stock with a cracking catalyst of the silica-alumina type at temperatures usually ranging from 500 to 950° F., the catalyst being maintained at high activity by frequent regeneration, to effect the conversion of some of the olefinic molecules to paraffins and of other olefinic molecules to aromatics without, however, producing substantial amounts of free hydrogen.

I have found that often the greater part of the C_5 olefins contained in the gasoline are destroyed by cracking, etc., in the retreating operation and do not undergo saturation to as great an extent as do the higher olefins. With this in mind, it is an object of my invention to substantially depentanize the olefinic gasoline before it is subjected to contact with the retreating catalyst in order that the C_5 olefins may be conserved and converted to more valuable products.

It is a further object of my invention to subject the C_5 fraction obtained from the depentanizing step to alkylation with isobutane to substantially completely saturate the olefins contained in this fraction by alkylation and to form a liquid product which is made up predominantly of residual C_5 paraffins (mostly isopentane), lower boiling paraffins, and products of the alkylation reaction. When this liquid product is blended in the proper proportions with the gasoline fraction obtained by retreating the depentanized olefinic gasoline charge, a suitable aviation gasoline stock may be obtained.

In one embodiment, the process of this invention comprises subjecting an olefinic gasoline containing C_5 olefins to a fractionation treatment to separate therefrom a liquid product substantially C_5 free and thereafter contacting said liquid product with a cracking catalyst to reduce the olefin content of said product.

In a more specific embodiment, the present invention comprises a process for preparing a gasoline fraction low in olefins from a gasoline fraction high in olefins and containing C_5 olefins which comprises fractionating the gasoline boiling range charging stock to separate a liquid product substantially free of C_5 and lower boiling hydrocarbons and a fraction consisting predominantly of C_5 and lower boiling hydrocarbons, contacting said liquid product with a cracking catalyst at conditions adequate to effect a substantial reduction in the olefin content thereof, subjecting the C_5 fraction to alkylation with isobutane to substantially completely react the olefins contained therein and blending at least a portion of the liquid fraction obtained from the alkylation treatment with gasoline boiling range hydrocarbons obtained from the olefin reduction treatment of said liquid product to prepare a gasoline having a low olefin content and a high lead response.

The accompanying flow drawing illustrates diagrammatically one particular form of the combination of steps which may be used in accomplishing the objects of this invention.

Referring now to the drawing, an olefinic gasoline such as that obtained from a catalytic cracking operation, and containing C_5 olefins, is supplied through line 1 to separation zone 2 wherein it is separated into various fractions. In the event that the gasoline is unstabilized, a C_2 and lighter fraction may be withdrawn through line 3. Furthermore, if the gasoline contains quantities of higher boiling hydrocarbons which would be unsatisfactory for further treatment, the higher boiling hydrocarbons may be withdrawn through line 4. A substantially depentanized gasoline fraction is also separated in zone 2 and withdrawn through line 5. A pentane-pentene fraction is separated and withdrawn through line 6. If C_3 and C_4 hydrocarbons are present in the charge, they may also be separated in zone 2, withdrawn from that zone through line 7 and if desired recovered as a product of the process through line 8. In order to effect the separation of the various hydrocarbon fractions, separation zone 2 may include the necessary fractionators, reboilers, condensers, and other auxiliary equipment conventionally used to obtain relatively narrow boiling hydrocarbon fractions.

The substantially depentanized gasoline withdrawn from zone 2 is supplied through line 5

to retreating zone 9 wherein it is contacted with a catalyst at conditions such that a substantial reduction in the olefin content of the gasoline is effected. Associations of silica with alumina magnesia or zirconia are usually employed as the catalyst, although other catalysts such as phosphoric acid may also be used at lower temperatures. The temperature in this zone may vary over a range of from 400 to 1000° F., preferably from 500 to 950° F., and the pressures from substantially atmospheric to 1000 pounds per square inch or more, the higher pressures usually being employed with the lower temperatures. Space velocities of from 0.2 to 8 unit weights of hydrocarbon charged per hour per unit weight of catalyst in the reaction zone are usually employed. The retreating zone may include the necessary heaters, reactors, regeneration equipment and other necessary equipment ordinarily used in this catalytic operation. In this zone the hydrocarbons to be treated may be passed upwardly through a turbulent bed of powdered catalyst in accordance with the "fluidized" technique recently developed, or they may be passed through a fixed bed of granular catalyst. In any event, the function of the retreating zone 9 is to substantially reduce the bromine number of the gasoline fraction charged thereto, and preferably to form a product, the normally liquid components of which have an olefin content as measured by the bromine number or iodine number of less than half that of the gasoline charged to this zone.

The products from retreating zone 9 are supplied through line 10 to separation zone 11 wherein, if the end-point of the liquid product is too high, a bottoms fraction may be removed through line 12. Light hydrocarbons, in some cases including C_5 hydrocarbons may be removed through line 13, while the greater portion of the products, namely the fractions boiling within the gasoline range, are removed through line 14. Separation zone 11 may include the necessary fractionators, stabilizers, etc., and other conventional equipment needed to effect the desired separation.

The C_5 hydrocarbons removed from zone 2 through line 6 are supplied together with, if desired, all or a portion of the C_3 and C_4 hydrocarbons removed from zone 2 through line 7, to the alkylation zone 15 wherein the olefins contained in the hydrocarbon fraction are alkylated with isobutane supplied through line 16. In some cases, a certain amount of the isoparaffins present in the C_4 and C_5 fractions will also be consumed in alkylating the olefins present in the same fractions. Usually, however, the greater part of the isopentane present in the C_5 fraction is not reacted in the alkylation zone and is therefore removed with the products of alkylation. Preferably the alkylation is conducted in the presence of a catalyst such hydrofluoric acid or sulfuric acid, although in some cases thermal alkylation may be used. The alkylation zone may include the necessary contactors, heat exchangers, fractionators, etc., to provide for the control of the reaction temperature and to maintain by means of internal recycling a high ratio of isobutane:olefin in order that the reaction will be selective.

The products of the reaction together with the unconverted paraffins present in the charging materials are removed from zone 15 through line 17 and supplied to separation zone 18 wherein, if necessary, a bottoms fraction may be separated from the product and removed through line 19. A light hydrocarbon fraction may be separated from the remainder of the product and removed through line 20. Separation zone 18 may include the necessary fractionators and stabilizers, etc., to accomplish this operation. The stabilized liquid product so obtained is removed from zone 18 through line 21.

In many instances, the proportion of C_5 hydrocarbons in the alkylate are such that on blending of the alkylate with the retreated fraction, aviation gasoline having the required 100 octane number with 4 cc. of tetraethyl lead per gallon may be obtained. In other operations, however, a portion of the alkylate and pentane fraction removed from zone 18 or a portion of the gasoline fraction removed from zone 11 may be withdrawn separately and the remaining alkylate and pentane fraction and gasoline fraction combined through lines 22 and 23. It is usually possible, however, to balance the operation so that the predominating portions of the liquid gasoline fractions removed from zones 11 and 18 may be combined to furnish a suitable aviation fuel.

The following example illustrates the advantage of employing the process of this invention when a catalytically cracked gasoline is to be retreated to form an aviation fuel stock.

Taking as a basis 1000 barrels of debutanized catalytically cracked gasoline, the relative proportions of the C_5 and higher boiling hydrocarbons in this fraction are as follows:

	Barrels
Pentenes	143
Pentanes	204
Hexanes and higher boiling hydrocarbons	653

If the 653 barrels of hexane and higher boiling hydrocarbons are contacted with a silica-alumina catalyst at 1.27 space velocity and 900° F. in a retreating operation to reduce the bromine number or, in other words, to reduce the olefin content of the fraction, a product distribution such as that shown below may be obtained:

Distribution of products from retreating

	Barrels
C_2, C_3 and C_4 hydrocarbons	55
Pentenes	15
Pentanes	27
Hexanes and higher boiling hydrocarbons	570

Overhead from depentanizing operation

	Barrels
Pentenes	143
Pentanes	204

It is evident from a comparison of these data with the data on the fractionation of the charge that a net gain of 15 barrels of pentenes and of 27 barrels of pentanes per thousand barrels of debutanized charge may be obtained.

On the other hand, if the entire debutanized charge material is retreated with the silica-alumina catalyst at substantially the same conditions to reduce the olefin content of the charge, the following distribution of product per 1000 barrels of debutanized charge is obtainable:

	Barrels
C_2, C_3 and C_4 hydrocarbons	118
Pentenes	74
Pentanes	222
Hexanes and higher boiling hydrocarbons	601

By comparing these data with the distribution of hydrocarbons in the charge, it is evident that although there is a slight net gain in the pentanes, there is an appreciable loss in the pentenes most of which are apparently cracked to lower boiling

hydrocarbons and, therefore, at least partially lost. On the other hand, if the charging material is first debutanized and then subjected to retreating, a net gain of C_5 hydrocarbons is obtainable and these C_5 hydrocarbons may be subjected to alkylation to further increase the yields of aviation quality gasoline that are obtainable by the process of this invention.

I claim as my invention:

1. A process for reducing the olefin content of an olefinic gasoline containing C_5 hydrocarbons which comprises separating said olefinic gasoline into a lower boiling fraction containing the C_5 hydrocarbons and a higher boiling fraction containing the C_6 and heavier hydrocarbons, subjecting said lower boiling fraction in admixture with an isoparaffin and at alkylating conditions to the action of an alkylating catalyst to form a product relatively free of olefins, subjecting said higher boiling fraction to the action of a siliceous catalyst at conditions of temperature and time of contact selected to effect conversion of said higher boiling fraction into a gasoline product of lower olefin content and blending the product of said alkylating step with the gasoline product from the last mentioned conversion step to form a full boiling range gasoline of low olefin content.

2. The process of claim 1 further characterized in that isobutane is supplied to the alkylating step.

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