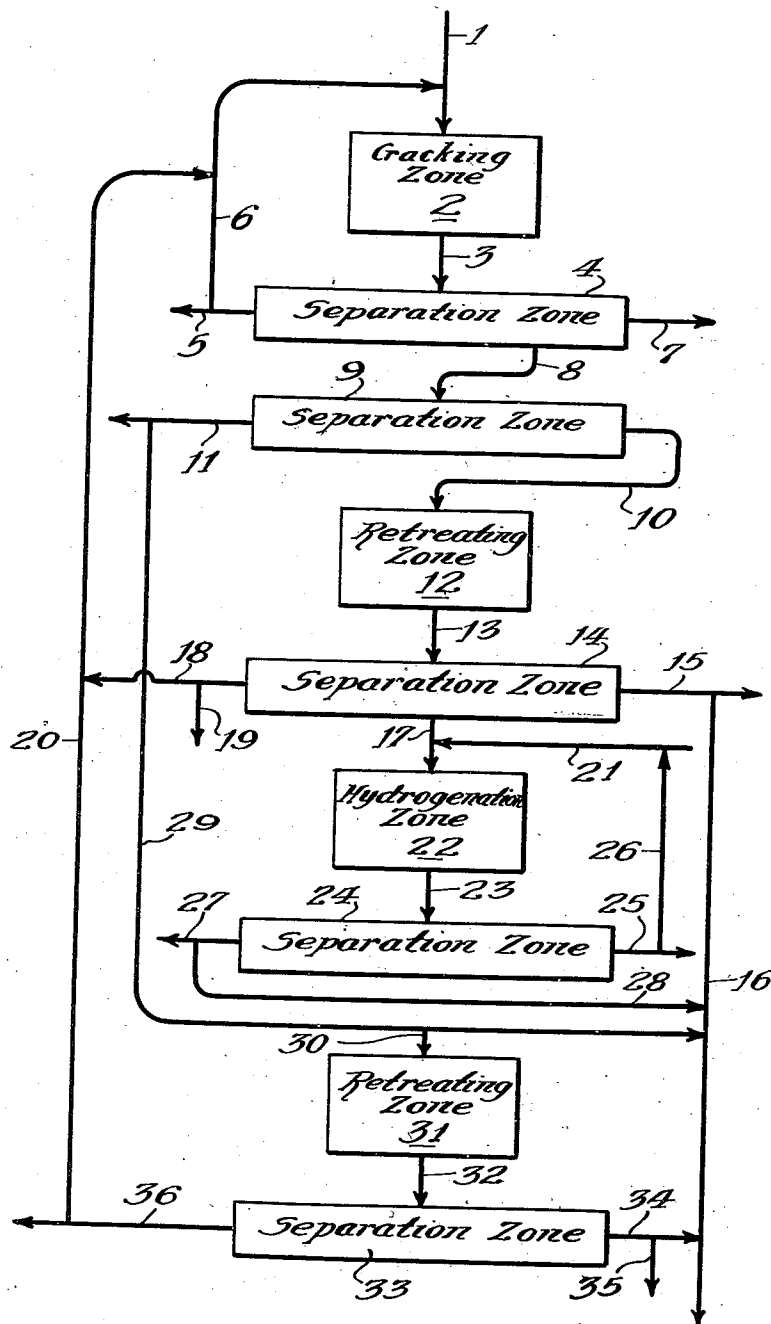


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TREATMENT OF HYDROCARBONS

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TREATMENT OF HYDROCARBONS

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This invention relates to the treatment of hydrocarbons and more particularly to a combination process comprising a series of interdependent and cooperative steps for the production of gasoline of high antiknock characteristics and low bromine number, which gasoline is particularly suitable for use in aviation fuel.

In a broad aspect the present invention relates to a process for producing gasoline of high antiknock characteristics and low bromine number, which comprises separating an olefinic gasoline into a light fraction and a heavy fraction, catalytically retreating the light fraction in the presence of a phosphoric acid catalyst to produce a retreated fraction of relatively low bromine number and at the same time forming olefinic hydrocarbons which are higher boiling than said light fraction, hydrogenating said olefinic hydrocarbons, and blending at least a portion of the hydrogenated products with said retreated fraction of relatively low bromine number.

In one specific embodiment the present invention relates to a process for the production of gasoline of high antiknock characteristics and low bromine number, which comprises subjecting oil to catalytic cracking to produce gasoline, separating the gasoline from normally gaseous hydrocarbons and from higher boiling insufficiently converted products, further separating said gasoline into a light fraction having an end boiling point within the range of from about 200° to about 300° F. and a heavy fraction having an initial boiling point within the range of from about 200° to about 300° F. and an end boiling point within the range of from about 300° to about 400° F., subjecting the light gasoline fraction to retreatment in the presence of a phosphoric acid catalyst under conditions to form a retreated light gasoline fraction having a lower bromine number and at the same time forming olefinic hydrocarbons having an initial boiling point above from about 200° to about 300° F., subjecting at least a portion of said olefinic hydrocarbons to hydrogenation to form paraffinic hydrocarbons, and blending at least a portion of said paraffinic hydrocarbons with at least a portion of said retreated light gasoline fraction of lower bromine number.

In accordance with the present invention, an olefinic gasoline fraction is subjected to retreatment in the presence of a phosphoric acid catalyst to form a retreated light gasoline fraction which is high in antiknock characteristics and low in bromine number. During such treat-

ment, a fraction boiling above the range of said retreated light fraction is formed and this higher boiling fraction is high in olefinic hydrocarbons. This higher boiling fraction is unsuitable for use in aviation gasoline because of its high olefin content and, as a feature of the present invention, it has been found that this higher boiling olefinic fraction may be subjected to hydrogenation to produce a substantially saturated product which is particularly suitable for blending with the retreated light gasoline fraction in order to form a final gasoline fraction of desired boiling range which is of exceptionally high antiknock characteristics, of relatively low bromine number and therefore particularly suitable for use in aviation gasoline.

The invention will be more fully described in connection with the attached diagrammatic flow drawing which illustrates several specific embodiments of the invention. It is understood, however, that the broad scope of the present invention is not limited to the particular embodiments illustrated in the drawing.

Referring to the drawing, the charging stock to the process may comprise any suitable oil, which usually will be heavier than gasoline, such as kerosene, gas oil, fuel oil and the like. The charging stock is introduced through line 1 and may be commingled with certain recycle streams in a manner to be hereinafter described in detail, and the commingled streams are supplied to cracking zone 2.

Cracking zone 2 may comprise any suitable cracking system for effecting the desired conversion of the oil into gasoline. While a non-catalytic operation may be employed in certain cases, in the preferred embodiment of the invention, zone 2 is preferably a catalytic cracking system. The catalytic cracking process may be of any suitable type and this may comprise the so-called fixed bed, fluidized, slurry, other types of moving beds, or combinations thereof. Any suitable cracking catalyst may be employed, the preferred catalyst comprising synthetically prepared composites of silica and alumina or other suitable metal oxides. These catalysts are normally utilized at temperatures within the range of 800° to 1200° F. and preferably within the range of 950° to 1050° F., superatmospheric pressures of below about 100 pounds per square inch and weight hourly space velocities which are usually above 1 and may in some cases be as high as 10 or even more. By weight hourly space velocity is meant the weight of oil per hour per weight of catalyst in the reaction zone. The

temperature, pressure, space velocity and the like are correlated in this step of the process to produce a gasoline of high antiknock characteristics. In order to obtain optimum conversions of the charging oil into gasoline of sufficiently high antiknock characteristics, the resulting gasoline will of necessity be of higher olefinic content than is permissible for use in aviation gasoline.

The cracked products are directed through line 3 into separation zone 4, which may comprise one or a plurality of suitable fractionating, absorbing or stripping zones, whereby the products introduced thereto may be separated into the desired fractions. In accordance with the preferred embodiment of the invention, hydrocarbons boiling from about 300° to about 400° F. are separated in zone 4 and are withdrawn from the lower portion thereof through line 5. These higher boiling products may be removed from the process or all or a portion thereof may be recycled by way of lines 6 and 1 to zone 2 for further conversion therein. Normally gaseous products may be withdrawn through line 7 from zone 4 and may be removed from the process. These gases are high in olefinic content and therefore are particularly suitable for use in subsequent polymerization, alkylation or other condensation reactions.

A gasoline fraction which, as heretofore set forth, will have an end boiling point within the range of from about 300° to about 400° F. and preferably in the neighborhood of 340° to 350° F., is withdrawn from zone 4 through line 8 and is directed into separation zone 9, which may be similar to heretofore described zone 4. In zone 9, the gasoline is separated into a light fraction which will have an end boiling point within the range of from about 200° to about 300° F. and preferably in the neighborhood of about 250° F., and a heavy gasoline fraction which will have an initial boiling point similar to the end boiling point of the light fraction and an end boiling point within the range of from about 300° to about 400° F. and preferably within the neighborhood of about 340° to about 350° F. The light fraction may be withdrawn from zone 9 through line 10 for further treatment in accordance with the present invention, as will be hereinafter described in detail, while the heavy gasoline fraction is withdrawn from the lower portion of zone 9 through line 11 for further treatment as will likewise be hereinafter described in detail.

The light gasoline fraction withdrawn through line 10 is directed into retreating zone 12. Retreating zone 12 may comprise any suitable system containing a phosphoric acid catalyst for reducing the bromine number of the light gasoline fraction introduced thereto while, at the same time, forming a higher boiling product which is olefinic in nature. According to the preferred embodiment of the invention, zone 12 comprises a retreatment zone in which the gasoline is contacted with an acid-acting compound of phosphorus at a temperature of from about 250° to about 750° F. and preferably of from about 350° to about 600° F. under sufficient pressure to maintain at least a substantial portion of the material in the reaction zone at the conditions of operation in liquid phase. Such a process is usually conducted at a weight hourly space velocity of from about 0.5 to about 10. Satisfactory but not necessarily equivalent catalysts include ortho-phosphoric acid, pyro-phosphoric acid, copper pyrophosphate, cadmium pyro-phosphate, etc., which may be employed either alone but preferably in

admixture with a suitable supporting material, such as kieselguhr, pumice, bentonite, bauxite, and other siliceous and aluminiferous materials, to form a solid phosphoric acid catalyst.

Another suitable method of operation, which is not necessarily equivalent to that heretofore described, is to subject the gasoline to contact with a silica base catalyst under selected conditions of operation. The silica base catalyst may be similar to or different than the preferred cracking catalyst employed in zone 2 and likewise is preferably synthetically prepared although certain natural occurring materials may be employed but not necessarily with equivalent results. These catalysts are usually employed at temperatures of between about 400° and about 700° F. under sufficient pressure to maintain at least a substantial portion of the material in the reaction zone in liquid phase. The weight hourly space velocities may be within the range of from about 0.3 to 5. The temperature, space velocity and other conditions of operation are correlated in order to produce a final gasoline product which is low in bromine number. Preferably, the bromine number is reduced to less than one-half that of the light gasoline fraction introduced through line 10 into zone 12.

The products from zone 12 are directed through line 13 into separation zone 14, which may be similar to heretofore described zones 4 or 9. In zone 14 a light gasoline fraction, which is high in antiknock characteristics and low in bromine number, is separated and is withdrawn therefrom through line 15 and may be removed from the process but preferably, in accordance with the features of the present invention, at least a portion thereof is directed through line 16 for blending with certain other products of the process in the manner to be hereinafter described in detail. This light fraction will have an end boiling point within the range of from about 200° to about 300° F. and preferably within the neighborhood of about 250° F.

As a feature of the present invention, an intermediate fraction boiling above the light gasoline fraction withdrawn through line 15 and having an end boiling point within the range of from about 300° to about 400° F. and preferably within the neighborhood of about 340° to about 350° F., is separated in zone 14 and is withdrawn therefrom through line 17. This intermediate fraction is too high in olefin content for use in aviation gasoline and, in accordance with the present invention, it is subjected to further treatment in the manner to be hereinafter described in detail. Hydrocarbons boiling above the intermediate fraction withdrawn through line 17 are separated in zone 14 and are withdrawn therefrom through line 18 and may be removed from the process through line 19, but preferably at least a portion thereof is directed by way of lines 20, 6 and 1 to zone 2 for further conversion therein.

The intermediate fraction withdrawn through line 17 is commingled with hydrogen introduced through line 21 and the mixture is directed into hydrogenation zone 22. The fraction supplied to zone 22 will contain aromatic hydrocarbons as well as olefinic hydrocarbons and hydrogenation in zone 22 is preferably regulated in order to substantially hydrogenate the olefinic hydrocarbons without substantial hydrogenation of the aromatic hydrocarbons. This may be readily accomplished by the use of particular catalysts and by controlling the conditions of operation. The

preferred catalyst comprises partially reduced nickel supported on a relatively inert carrier such as kieselguhr and the temperature employed is preferably below 400° F., although it is understood that higher temperatures may be employed if the other conditions of operation, such as space velocity and pressure, are correlated therewith in order to effect the desired reaction.

Hydrogenation zone 22 may comprise any suitable hydrogenation system which may be of the fixed bed or moving catalyst type. In the fixed bed type of process, usually two or more zones are employed with counter-current flow of hydrogen and hydrocarbons, although a single zone may be utilized when desired.

The hydrogenated products are directed from zone 22 through line 23 into separation zone 24 which may be similar to heretofore described zones 4, 9 or 14. Since an excess of hydrogen is usually employed in the hydrogenation reaction, unused hydrogen may be withdrawn through line 25 from zone 24 and may be removed from the process but preferably at least a portion thereof is recycled by way of lines 26, 21 and 17 to zone 22 for further use therein. The hydrogenated products are withdrawn from the lower portion of zone 24 through line 27 and a portion thereof may be removed from the process while, in accordance with the present invention, at least a portion thereof is directed by way of line 28 into line 16 wherein it is commingled with at least a portion of the light retreated gasoline withdrawn through line 15 from zone 14. It has been found that blending of the hydrogenated products with the light gasoline retreated fraction, in the manner herein described, produces a gasoline product of exceptionally high antiknock characteristics and of low bromine number which is particularly suitable for use in aviation gasoline.

The heavy gasoline fraction separated in zone 9 and withdrawn therefrom through line 11 may be directed, all or in part, through line 29 and may be commingled with the final gasoline products in line 16. The heavy gasoline fraction withdrawn through line 11 will be high in aromatic content and in many cases will be sufficiently low in bromine number, so that it may be blended without further treatment with the other products of the process in order to increase the yield of desired aviation gasoline. In some cases, it is preferred to subject the heavier gasoline fraction to further treatment and this may be accomplished by supplying the same through lines 29 and 30 into retreating zone 31. Retreating zone 31 may be similar to heretofore described zone 12 and may utilize a similar type of catalyst. The temperature employed in zone 31 may be the same or slightly higher than that employed in zone 12 in order to effect the desired reduction in bromine number and other improvements.

The products from zone 31 are then directed through line 32 into separation zone 33 which may be similar to the heretofore described separation zones. A retreated gasoline fraction having an end boiling point within the range of from about 300° to about 400° F., which end boiling point is preferably the same as the end boiling point of the gasoline in line 16, may be separated in zone 33 and withdrawn therefrom through line 34. A portion thereof may be removed from the process through line 35 but preferably all or a portion of this gasoline is directed through line 34 and is commingled in line 16 with the final gasoline product of the process. In this way, ad-

ditional yields of the desired gasoline products are obtained.

Higher boiling products are separated in zone 33 and withdrawn therefrom through line 36 and may be removed from the process but preferably at least a portion thereof is directed by way of lines 20, 6 and 1 into cracking zone 2 for further conversion therein.

The following example is introduced for the purpose of further illustrating the novelty and utility of the present invention but not with the intention of unduly limiting the same.

A Mid-Continent gas oil is cracked in the presence of a silica-alumina catalyst at a temperature of about 950° F. and an hourly weight space velocity of about 1.7. The products are separated by conventional fractionation into a light gasoline fraction having an end boiling point of 250° F. and a heavy gasoline fraction having an initial boiling point of 250° F. and an end boiling point of 350° F.

The light gasoline fraction is subjected to retreatment in the presence of a solid phosphoric acid catalyst at a temperature of 525° F. and 600 pounds per square inch, the solid phosphoric acid catalyst comprising a mixture of ortho and pyro phosphoric acids composited with kieselguhr. The retreated products are separated into a light fraction having an end boiling point of 250° F., an intermediate fraction having an initial boiling point of 250° F. and an end boiling point of 350° F., and heavier products.

The intermediate fraction is subjected to hydrogenation in the presence of a reduced nickel-kieselguhr catalyst at a temperature of about 250° F. A light fraction having an end boiling point of about 350° F. is separated from the hydrogenated products and is blended with the retreated light gasoline fraction.

The blended products have a relatively low bromine number and exceptionally good antiknock characteristics. Upon the addition of 4 cc. of tetraethyl lead, and other additives usually employed for the production of aviation gasoline, the finally blended material has an octane number of above 100 when determined according to the motor method.

I claim as my invention:

1. A hydrocarbon conversion process which comprises treating an olefinic gasoline with a phosphoric acid catalyst under conditions to produce a light gasoline fraction of low bromine number and a heavy olefinic fraction of higher bromine number, hydrogenating at least a portion of said heavy olefinic fraction, and blending at least a portion of the hydrogenated products with said light gasoline fraction of low bromine number.

2. A hydrocarbon conversion process which comprises treating cracked gasoline with a phosphoric acid catalyst under conditions to produce a light gasoline fraction of low bromine number and having an end boiling point within the range of from about 200° to about 300° F., and a heavy olefinic fraction of higher bromine number having an initial boiling point within the range of from about 200° to about 300° F. and an end boiling point within the range of from about 300° to about 400° F., catalytically hydrogenating at least a portion of said heavy olefinic fraction, and blending at least a portion of the hydrogenated products with said light gasoline fraction to produce a final gasoline product having a bromine number of less than one-half that of said cracked gasoline.

3. A hydrocarbon conversion process which comprises cracking oil under conditions to produce a cracked gasoline of high antiknock characteristics and high bromine number, separating said gasoline into light and heavy fractions, retreating said light fraction in the presence of a phosphoric acid catalyst under conditions to produce a light gasoline fraction of low bromine number and a heavier olefinic fraction of higher bromine number, catalytically hydrogenating said heavier olefinic fraction in the presence of added hydrogen, and blending at least a portion of the hydrogenated products with said light gasoline fraction of low bromine number.

4. The process of claim 3 further characterized in that at least a portion of the first mentioned heavy fraction is blended with the retreated and hydrogenated products.

5. The process of claim 3 further characterized in that at least a portion of first mentioned heavy fraction is subjected to separate retreatment in the presence of a phosphoric acid catalyst, and at least a portion of the separately retreated products is blended with the first mentioned retreated and hydrogenated products.

6. A hydrocarbon conversion process which comprises catalytically cracking oil under conditions to produce a cracked gasoline of high antiknock characteristics and high bromine number, separating said gasoline into a light fraction having an end boiling point within the range of from about 200° to about 300° F. and a heavy gasoline fraction having an initial boiling point within the range of from about 200° to about 300° F. and an end boiling point within the range of from 300° to about 400° F., retreating said light fraction in the presence of a phosphoric acid catalyst under conditions to produce a light gasoline fraction of low bromine number and having an end boiling point within the range of from about 200° to about 300° F. and a heavier olefinic fraction of higher bromine number having an initial boiling point within the range of from about 200° to about 300° F. and an end boiling point within the range of from about 300° to about 400° F., hydrogenating said heavier olefinic fraction in the presence of a nickel hydrogenating catalyst and hydrogen, separating a fraction having an end boiling point within the

range of from about 300° to about 400° F. from the hydrogenated products and blending at least a portion thereof with said light gasoline fraction of low bromine number.

7. A process for producing hydrocarbon distillate suitable for use in aviation fuel from the products of hydrocarbon oil cracking, which comprises separating from said products an olefinic gasoline fraction having an end boiling point in the approximate range of 200° F. to 300° F., contacting said gasoline fraction with a catalyst comprising an acid-acting compound of phosphorus at a temperature of from about 250° F. to about 750° F. and at a weight hourly space velocity of from about 0.5 to about 10, whereby to reduce the bromine number of said fraction and form a heavier olefinic fraction, separating said heavier olefinic fraction from the lower boiling gasoline fraction of reduced bromine number and hydrogenating at least a portion thereof to form paraffinic hydrocarbons, and blending at least a portion of said paraffinic hydrocarbons with at least a portion of said gasoline fraction of reduced bromine number.

8. A process for improving cracked gasoline which comprises separating the same into a light olefinic fraction and a heavier gasoline fraction, contacting said light fraction with a catalyst comprising an acid-acting compound of phosphorus at a temperature of from about 250° F. to about 750° F. and at a weight hourly space velocity of from about 0.5 to about 10, whereby to reduce the bromine number of said fraction and form a heavier olefinic fraction, separating said heavier olefinic fraction from the lower boiling gasoline fraction of reduced bromine number and hydrogenating at least a portion thereof to form paraffinic hydrocarbons, and blending regulated portions of said paraffinic hydrocarbons, said heavier gasoline fraction and said gasoline fraction of reduced bromine number.

9. The process as defined in claim 8 further characterized in that said heavier gasoline fraction is catalytically treated for reduction in bromine number prior to the blending thereof with said paraffinic hydrocarbons and gasoline fraction of reduced bromine number.

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