Aug. 14, 1945. J. T. PINKSTON, JR 2,382,910

CONVERSION OF HYDROCARBONS

Filed Nov. 27, 1942

Fig. 1.

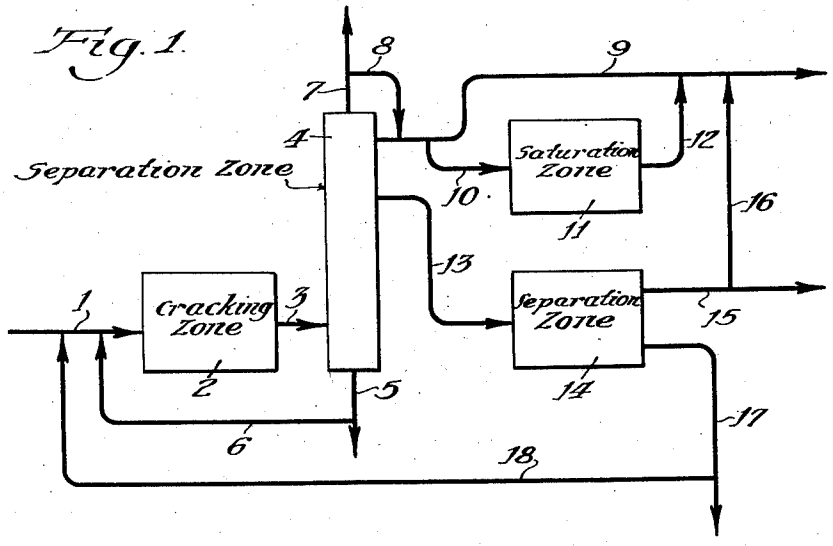
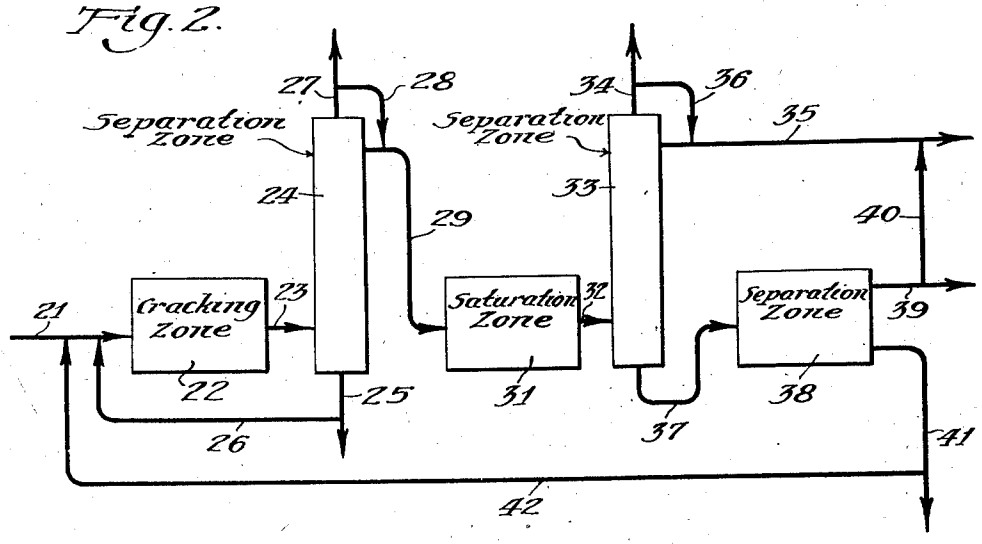


Fig. 2.



Inventor:
John T. Pinkston, Jr.
By Lacey J. Daniel
Attorney.

Patented Aug. 14, 1945 2,382,910

UNITED STATES PATENT OFFICE

2,382,910

CONVERSION OF HYDROCARBONS

John T. Pinkston, Jr., Riverside, Ill., assignor to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

Application November 27, 1942, Serial No. 467,103

2 Claims. (Cl. 196—52)

This invention relates particularly to the production of aviation base gasoline by a series of cooperative and interdependent steps. In addition to the production of aviation gasoline, selected alkylated aromatic hydrocarbons such as toluene, xylene, ethylbenzene, etc. may be recovered as products of the process.

In its broadest scope, the invention comprises the separation of a saturated cracked gasoline into selected low and high boiling fractions, treating the high boiling fractions to separate and recover aromatic hydrocarbons therefrom, and blending regulated portions of the aromatic hydrocarbons with said low boiling fractions to produce saturated gasoline of high antiknock value which is particularly suitable for use in aviation gasoline.

In one specific embodiment the present invention comprises a process for the production of aviation gasoline by subjecting oil heavier than gasoline to cracking in the presence of a catalyst and under conditions to produce a substantially saturated gasoline product, fractionating said gasoline product to separate a light fraction having an end-point between about 175° to about 250° F. and a heavier fraction boiling above the light fraction and having an end-boiling point in the range of from about 275° to about 350° F., treating said heavier fraction to separate aromatic from non-aromatic hydrocarbons, and blending regulated portions of the thus separated aromatic hydrocarbons with said light fraction to produce a high antiknock gasoline which is particularly suitable for use in aviation gasoline.

Another specific embodiment of the invention comprises a process for the production of aviation gasoline by subjecting oil to cracking under conditions to produce an olefinic gasoline, fractionating the gasoline to separate a light fraction having an end-point between about 175° to about 250° F. and a heavier fraction boiling above the light fraction and having an end boiling point in the range of from about 275° to about 350° F., subjecting said light fraction to treatment in the presence of a catalyst and under conditions to substantially saturate the olefinic hydrocarbons contained therein, treating said heavier fraction to separate aromatic from non-aromatic hydrocarbons, and blending regulated portions of the thus separated aromatic hydrocarbons with said light fraction to produce a high antiknock gasoline which is particularly suitable for use in aviation gasoline.

Another specific embodiment of the invention comprises a process for the production of aviation gasoline by subjecting oil to cracking under conditions to produce an olefinic gasoline, subjecting the products of said cracking to treatment to separate a gasoline fraction having an end-boiling point in the range of from about 275° to about 350° F., subjecting said gasoline fraction to treatment in the presence of a catalyst and under conditions to substantially saturate the olefins contained therein, fractionating the saturated products to separate a light fraction having an end-point between about 175° to about 250° F. and a heavier fraction, treating said heavier fraction to separate aromatic from non-aromatic hydrocarbons, and blending regulated portions of the thus separated aromatic hydrocarbons with said light fraction to produce a high antiknock gasoline which is particularly suitable for use in aviation gasoline.

As one of the particular advantages of the present invention, experiments have indicated that, while ethyl and methyl groups are removed from the aromatic nuclei only with great difficulty in the catalytic cracking step, alkyl groups containing more than two carbon atoms are very easily cracked off, the rupture taking place at the point of junction of the alkyl group with the nucleus. This facilitates the subsequent separation of the aromatic hydrocarbons, since the greater portion of the aromatic hydrocarbons will be methyl and ethyl substituted and thus the separation step will not be complicated by the presence of large amounts of higher boiling aromatic hydrocarbons. Thus, the higher boiling aromatic hydrocarbons are cracked to produce lower boiling aromatic hydrocarbons and these lower boiling aromatic hydrocarbons are subsequently separated from the non-aromatic hydrocarbons, and the lower boiling aromatic hydrocarbons are finally blended with the light gasoline fraction to produce aviation gasoline. This cooperative treatment of the high boiling aromatic hydrocarbons in the series of interrelated steps of the present invention produces the improved final gasoline product of the process which is not readily obtained by other means.

The invention will be more fully explained in connection with the accompanying diagrammatic flow drawing.

Figure 1 illustrates several embodiments of the invention and Figure 2 illustrates still another embodiment of the invention. It will be understood, however, that various modifications may be made within the broad scope of the present invention.

Figure 1 of the drawing will be described in

connection with a process in which a substantially saturated gasoline is produced in the cracking step of the process. In this operation, the charging stock will be introduced to the process through line 1 and will be directed into cracking zone 2. Cracking zone 2 will comprise a catalytic cracking operation which usually will be conducted at a temperature of from about 600° to about 1000° F. and preferably of from about 750° to about 950° F. A moderately superatmospheric pressure is usually employed, although higher pressures up to 1000 pounds or more may be used, if desired. The hourly weight space velocity, defined as the weight of oil per hour per weight of catalyst in the reactor, will usually be within the range of from about 0.25 to about 5 and preferably of from about 0.5 to about 2.

Any suitable catalyst may be employed, particularly satisfactory catalysts including catalysts of the silica base type in which silica is composited with alumina, zirconia, thoria or other suitable metal oxides, or mixtures thereof. These catalysts may be either of natural origin or they may be prepared synthetically by any suitable method. It is understood that the results obtained by the use of different operating conditions will not necessarily be equivalent.

The cracking operation may be of the fixed bed, fluid or slurry type and may utilize any suitable apparatus to effect the desired conversion in a manner well known in the art.

The products from cracking zone 2 are directed through line 3 into separation zone 4. Separation zone 4 may comprise one or a plurality of suitable separating, fractionating, distilling, absorbing and/or stripping zones whereby the products introduced thereto may be separated into the desired fractions. The products introduced into zone 4 may be separated therein into a normally gaseous fraction, a light gasoline fraction having an end-boiling point of from about 175° to about 250° F., and a heavier gasoline fraction boiling above the light gasoline fraction and having an end-boiling point of about 275° to about 350° F., as well as higher boiling material. In the case here illustrated, the materials boiling above about 350° F. are condensed in zone 4 and removed from the lower portion thereof through line 5. This stream may be withdrawn 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.

The normally gaseous fraction separated in zone 4 may be withdrawn from the upper portion thereof through line 7 to storage or any further desired treatment. When desired the light gasoline fraction separated in zone 4 may be withdrawn from the upper portion thereof together with the normally gaseous components and, in this case, this stream would be directed through lines 8 and 9 for blending in a manner to be hereinafter described in detail. In another operation the normally gaseous components may be withdrawn through line 7, and the light gasoline fraction may be withdrawn through line 9 for the subsequent blending treatment.

The higher boiling gasoline fraction may be withdrawn from zone 4 through line 13 and directed to separation zone 14. Separation zone 14 may comprise any suitable process to effect separation of the aromatic hydrocarbons from the non-aromatic hydrocarbons. One of the preferred methods for accomplishing this separation is by azeotropic distillation. Any suitable azeotrope forming material may be employed, including acetic acid, ethyl alcohol, mono-methyl-ether of ethylene glycol, furfural, etc. The process is usually conducted at a temperature in the neighborhood of from about 200° to about 250° F. and under substantially atmospheric pressure. This temperature is dependent, of course, on the choice of azeotrope forming agent. If higher pressures are employed the temperature should be modified accordingly.

Another suitable method for effecting this separation is by the use of solvent extraction. Any suitable solvent may be employed including, for example, aniline, liquid sulfur dioxide, furfural, etc.

Whichever type of separation process is employed, the aromatic hydrocarbons may be withdrawn from zone 14 through line 15 and, in accordance with the present invention, at least a portion of these aromatic hydrocarbons are directed through line 16 and commingled with the light gasoline fraction previously separated and withdrawn through line 9. By blending regulated amounts of the aromatic hydrocarbons with the light gasoline fraction, I have found that the antiknock value of the total gasoline product is greatly improved and, according to the features of the present invention, a substantially saturated product is obtained which product, being of high antiknock value and substantially saturated in character, is particularly suitable for use in aviation gasoline.

It is also within the scope of the invention, when desired, to fractionate or otherwise treat the aromatic hydrocarbon withdrawn through line 15 to separate individual aromatic hydrocarbons such as benzene, toluene, xylenes, ethyl benzene, etc., and to recover regulated portions thereof, while utilizing the remaining aromatic hydrocarbons for blending in the manner hereinbefore described.

As heretofore described, the higher boiling aromatic hydrocarbons are decomposed in the cracking step of the process to produce lower boiling aromatic hydrocarbons. This is particularly applicable in case it is desired to recover individual aromatic hydrocarbons. For example, if it is desired to recover xylenes, the higher boiling aromatics are decomposed into large yields of xylenes and the xylenes may then be recovered from the separation step of the process. This separation is facilitated in view of the fact that large amounts of higher boiling aromatic hydrocarbons are not present to complicate the separation process.

The non-aromatic hydrocarbons are withdrawn from zone 14 through line 17 and may be removed from the process. When desired, all or a portion of the non-aromatic hydrocarbons may be recycled by way of lines 18 and 1 to zone 2 for further conversion in the process.

The above description is directed to a process in which a substantially saturated gasoline is produced in the cracking step of the process. The following description is directed to a process in which an olefinic type of gasoline is produced in the cracking step of the process as also illustrated in Figure 1 of the drawing.

The charging stock is introduced through line 1 into cracking zone 2. In this case cracking zone 2 may comprise either a non-catalytic or a catalytic operation. Non-catalytic cracking is usually effected at temperatures of from about 800 to about 1200° F. under substantially atmospheric pressure up to superatmospheric pressures of 1000 pounds or more. Catalytic cracking is usually

effected at a temperature of from about 800° to 1200° F., moderately superatmospheric pressure and an hourly weight space velocity of from about 0.25 to about 10 and usually of from about 1 to about 4. Any suitable catalyst may be employed including those heretofore described. It is understood that the results obtained by these various catalysts and by the use of the various conditions of operation will not necessarily be equivalent.

The cracked products are directed through line 3 to zone 4 and are therein separated in a manner similar to that heretofore described. The light gasoline fraction, either with or without normally gaseous hydrocarbons, is directed through lines 9 and 10 into saturation zone 11. Saturation zone 11 may comprise any suitable apparatus wherein the olefins contained in said light gasoline fraction undergo substantial saturation. One suitable method comprises subjecting the olefinic fraction to treatment with a silica base catalyst of the type heretofore described, under substantially the same range of conditions previously described in connection with the conversion to produce a substantially saturated gasoline but usually at the lower temperatures. These conditions will, in any event, be controlled in order to convert the olefinic hydrocarbons by reactions including hydrogen transfer into non-olefinic hydrocarbons in the gasoline boiling range. Other suitable and well known hydrogen transfer operations may alternatively be employed but not necessarily with equivalent results. Still another suitable but not necessarily equivalent methods of operation is by direct hydrogenation of the olefinic compounds in the presence of suitable hydrogenation catalysts including for example reduced nickel, copper, etc.

The products from saturation zone 11 are then directed through line 12 into line 9 for subsequent blending in a manner to be hereinafter described in detail. It is, of course, understood that zone 11 may include suitable means to separate unconverted reactants and to recycle the unconverted material back to the process for further conversion when desired. This has not been illustrated in the drawing in the interest of simplicity.

The higher boiling gasoline fraction is supplied through line 13 into separation zone 14 for treatment in the manner heretofore described, and, in accordance with the present invention, at least a portion of the separated aromatic hydrocarbons are blended with the light gasoline fraction.

Figure 2 illustrates another embodiment of the invention in which an olefinic type of gasoline is produced in the cracking step. Referring to Figure 2, the charging stock is introduced through line 21 into cracking zone 22 which may be either of the catalytic or non-catalytic type. This zone will operate in a manner similar to that heretofore described in connection with the production of an olefinic gasoline in zone 2. The products from zone 22 are directed through line 23 into separation zone 24 which will be similar to separation zone 4. The higher boiling products are withdrawn from zone 24 through line 25 and all or a portion thereof may be recycled by way of lines 26 and 21 to cracking zone 22.

In this operation, normally gaseous hydrocarbons may be separated and withdrawn through line 27, while a gasoline fraction having an end-boiling point of between about 275° to about 350° F. is withdrawn through line 29, and is directed into saturation zone 31. When desired, the normally gaseous hydrocarbons may be retained in the light gasoline fraction and the mixture may be withdrawn through line 27, the mixture then being directed through lines 28 and 29 into zone 31.

Zone 31 will be similar in character to zone 11 hereinbefore described, and the substantially saturated products withdrawn from zone 31 are directed through line 32 into separation zone 33. In case the normally gaseous products were not previously separated in zone 24, these gases may be separated in zone 33 and withdrawn from upper portion thereof through line 34, when desired. In this case, a light gasoline fraction having an end-boiling point of between about 175° to about 250° F. is withdrawn from zone 33 through line 35. It is also within the scope of the invention to withdraw a mixture of gases and light gasoline through line 34 and direct the same through line 36 into line 35 for subsequent blending treatment in accordance with the features of the invention.

The heavy gasoline fraction having an end-boiling point of from about 275° to about 350° F. is withdrawn from the lower portion of zone 33 through line 37 and is directed into separation zone 38. Zone 38 will be similar to zone 14 as heretofore described. The aromatic hydrocarbons may be withdrawn from zone 38 through line 39 and all or a portion thereof are directed through line 40 for blending with the light gasoline fraction in the manner heretofore described. It is also within the scope of the invention to separate and recover selected aromatic hydrocarbons from this step of the process in the manner previously described in connection with another embodiment of the invention. Non-aromatic hydrocarbons are withdrawn from zone 38 through line 41 and all or a portion thereof may be recycled through lines 42 and 21 to zone 22 for further conversion therein.

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

An East Texas gas oil may be subjected to catalytic cracking in a fluid type of operation at a temperature of 900° F. to yield 30% by volume per pass of substantially saturated gasoline. The gasoline may be further fractionated to separate the same into a light fraction having an end-boiling point of 240° F. and a heavy gasoline fraction having an end-boiling point of 318° F. The heavy gasoline fraction may be subjected to azeotropic distillation in the presence of acetic acid at a temperature of from 220° to 244° F. to yield an overhead non-aromatic fraction and to leave a bottom aromatic fraction, the split being substantially even; that is, the aromatic fraction and the non-aromatic fraction will each comprise about 50% of the charge to the azeotropic distillation step. Upon analysis, these fractions will show that the aromatic fraction has an octane number equivalent to isooctane plus 0.1 cc. of tetraethyl lead and that the non-aromatic fraction will have an octane number of 57.9 by the motor method. Regulated portions of the aromatic hydrocarbons are then blended with the light gasoline fraction in order to produce a final product of high antiknock value and substantially saturated in character for use in aviation gasoline.

It is apparent, from the above example, that the non-aromatic hydrocarbons in the higher boiling fraction of the gasoline greatly lowers the octane number of the full boiling range gasoline.

According to the feature of the present invention, regulated portions of the aromatic hydrocarbons having a higher octane value than the light fraction, are blended with the light fraction to produce a final product having a higher octane value than is otherwise readily obtainable.

I claim as my invention:

1. A hydrocarbon conversion process which comprises cracking a hydrocarbon oil to produce an olefinic gasoline, fractionating the products of said cracking to separate a gasoline fraction having an end-point below about 350° F., subjecting said gasoline fraction to treatment in the presence of a catalyst to substantially saturate the olefinic compounds contained therein and to thereby produce a substantiatlly olefin free gasoline product, fractionating the substantially olefin free gasoline product to separate a light gasoline fraction having an end-point below about 250° F. and a heavier fraction containing components boiling above said light fraction having an end-boiling point below about 350° F., separating said heavier fraction into an aromatic concentrate and a non-aromatic concentrate, and blending at least a portion of said separated aromatic concentrate with said light gasoline fraction.

2. A process for producing aviation gasoline from cracked gasolines containing olefins and aromatics which comprises subjecting the cracked gasoline to the action of a siliceous cracking catalyst at a temperature of from about 600° F. to about 1000° F., and at a weight hourly space velocity of from about 0.25 to about 5, whereby to produce a substantially olefin-free gasoline product, separating the resultant substantially olefin-free gasoline product into a light gasoline fraction having an end boiling point not in excess of 250° F. and a heavier fraction having an end boiling point not in excess of 350° F., separating said heavier fraction into an aromatic concentrate and a non-aromatic concentrate, and blending at least a portion of said aromatic concentrate with said light gasoline fraction to form a high anti-knock gasoline.

JOHN T. PINKSTON, JR.