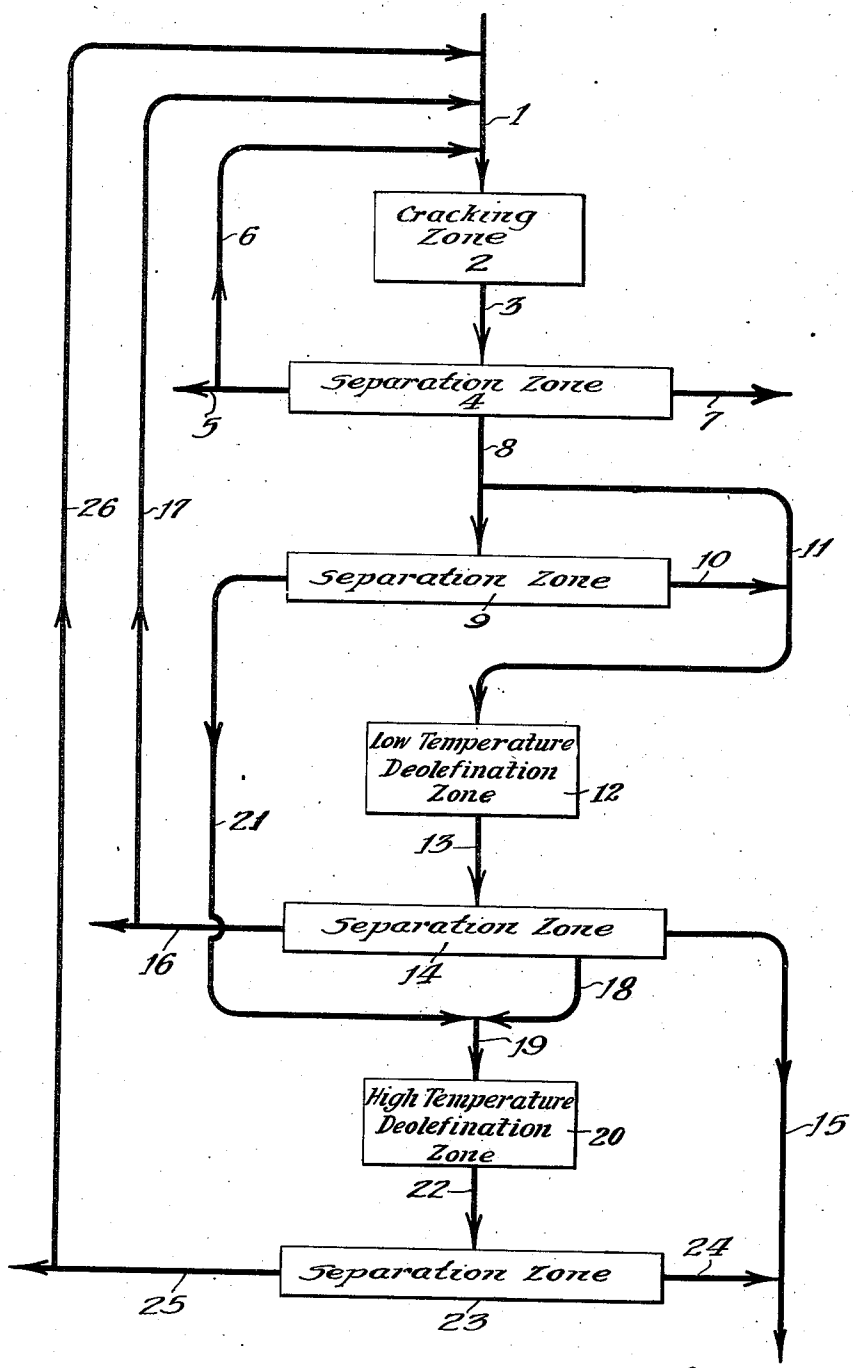
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CONVERSIONS OF HYDROCARBONS

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Inventors:
Vladimir Haensel
Vladimir N. Ipatieff
By: Lee J. Sarg
Attorney.

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CONVERSIONS OF HYDROCARBONS

Vladimir Haensel and Vladimir N. Ipatieff, Riverside, Ill., assignors to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

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This invention relates particularly to an improved process for reducing the bromine number of gasolines containing unsaturated hydrocarbons. Cracked or reformed gasolines, although having a relatively high initial octane number, are usually unsuitable for use in aviation fuel because of their high olefin content and relatively low lead susceptibility. The present invention is directed to an improved method of reducing the bromine number of such gasolines.

The bromine number of unsaturated gasolines may be reduced to less than half, with a resultant increase in lead susceptibility, by contacting the gasoline with certain catalysts under specific conditions of operation. One suitable method, which we have previously disclosed, is treating the gasoline with an acid-acting oxygen compound of phosphorus at a temperature of from about 250° F. to about 750° F. and preferably of from about 350° F. 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 process is usually conducted at a space velocity of from about 0.5 to about 10, the space velocity being defined as the weight of charge per hour per unit weight of catalyst in the reaction zone. Satisfactory but not necessarily equivalent catalysts include orthophosphoric acid, pyro-phosphoric acid, copper pyro-phosphate, cadmium pyro-phosphate, etc. which may be employed either alone or in admixture with a suitable supporting material, such as kieselguhr, pumice, bentonite, bauxite, and other siliceous and aluminiferous materials.

Another suitable method of operation is to subject the gasoline to contact with a silica base catalyst under selected conditions of operation. The silica base catalysts comprise various associations of silica with one or more compounds of elements whose oxides are refractory, such as alumina, zirconia, magnesia, thoria, ceria, etc. These catalysts may be synthetically prepared. Certain natural occurring materials, such as bentonite, montmorillonite, floridin, etc. may be used but not necessarily with equivalent results. These catalysts are usually employed at a temperature of below 1000° F. and more generally at a temperature of below 900° F., and in one method of operation are used at a temperature of between about 400° F. 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 space velocities in this method of operation will ordinarily be within the range of from about 0.3 to about 15.

We have now found that improved results in the foregoing general processes may be obtained by subjecting the gasoline to a two-stage treatment, that is, subjecting the heavier and lighter fractions of the gasoline to treatment under different conditions of operation. This improved process may be conducted by first separating the gasoline into light and heavy fractions and then subjecting each fraction to separate treatment with the catalyst under different conditions of operation, followed by blending of the desired gasoline fractions. In another method of operation the full boiling range gasoline may be subjected to treatment with the catalyst, the resultant products separated into light and heavy fractions, the heavy fractions subjected to a separate treatment in the presence of a catalyst under more severe conditions of operation, and blending of the desired fractions of the products of both steps of the process.

The exact reasons for the improved results obtained by the two-stage process of the present invention are not completely known, but it is believed that the olefins present in the lower boiling fraction of the gasoline are in part transformed into higher boiling hydrocarbons. If a higher temperature is used originally in the treatment of the full boiling range gasoline, the carbon formation is excessive and may negative the commercial importance of the process. On the other hand, if the full boiling range gasoline charging stock is given a second treatment at the higher temperatures the lower boiling saturated hydrocarbon has a dilution effect. In addition, it is desired in most cases to maintain a liquid phase in the reaction zone since our experiments have indicated that considerably less carbon formation occurs with liquid phase operations as compared to vapor phase operations. The presence of large amounts of lighter hydrocarbons preclude the treatment of the charging stock in liquid phase at the higher temperatures.

Thus, the present invention offers an improved process for reducing the bromine number of unsaturated cracked gasolines with increased yield, lower bromine number, and less carbon formation than is otherwise obtainable.

In one specific embodiment, the present invention relates to a process for reducing the bromine number of an unsaturated cracked gasoline which comprises separating said gasoline into a light fraction and a heavy fraction, subjecting the light fraction to contact with a suitable catalyst at a temperature of from about 400° F. to about 550° F. under sufficient pressure to maintain at

least a portion of the hydrocarbons in the reaction zone in liquid phase, separately subjecting the heavy fraction to contact with a suitable catalyst at a temperature of from about 480° F. to about 700° F. under sufficient pressure to maintain at least a portion of the hydrocarbons in the reaction zone in liquid phase, separating material boiling within the desired range from the products of both reactions, and blending regulated portions of said material to produce a final product having a bromine number of less than half that of said unsaturated cracked gasoline.

In another specific embodiment, the invention relates to a process for reducing the bromine number of an unsaturated cracked gasoline which comprises subjecting said gasoline to treatment with a suitable catalyst at a temperature of from about 400° F. to about 550° F. under sufficient pressure to maintain at least a portion of the hydrocarbons in the reaction zone in liquid phase, separating the resultant products into light and heavy gasoline fractions, subjecting said heavy fraction to separate treatment with a suitable catalyst at a temperature of from about 480° F. to about 700° F. under sufficient pressure to maintain at least a portion of the hydrocarbons in the reaction zone in liquid phase, separating material boiling within the desired range from the products of both reactions, and blending regulated amounts thereof to produce a final product having a bromine number of less than half that of said unsaturated cracked gasoline.

The invention will be further explained in connection with the accompanying flow diagrammatic drawing which illustrates several manners in which the process may be conducted.

The invention is described in conjunction with a cracking operation which may be either catalytic or noncatalytic. If aviation gasoline is desired as the final product of the process and the charging stock to the process comprises a material boiling above the range of gasoline, it is usually preferred that the cracking step be catalytic. It is understood that, instead of cracking, a reforming operation may be utilized when the charging stock of the process is a material boiling substantially within the range of gasoline, and the reforming operation may be either catalytic or non-catalytic.

Referring to the drawing, the charging stock is introduced to the process through line 1 and may be commingled with certain recycle streams in a manner to be hereinafter described in detail, and the commingled material is supplied to cracking zone 2. Any suitable cracking or reforming process and any suitable cracking or reforming catalyst, when employed, may be utilized in zone 2.

The cracked products are directed through line 3 into separation zone 4. This separation zone may comprise one or a plurality of suitable flashing, fractionating, absorbing, or stripping zones, whereby the products introduced thereto may be separated into the desired fractions. Material boiling above the range of gasoline alone or, in certain cases, together with higher boiling gasoline fractions such as those boiling above 300° or 350° F., are withdrawn from the lower portion of zone 4 through line 5 and may be removed from the process. Preferably, however, at least a portion of this material is recycled by way of lines 6 and 1 to zone 2 for further conversion therein. Process gases, which may or may not include butane, as desired, are withdrawn from zone 4 through line 7 to storage or further treatment, as desired.

The desired gasoline fraction is withdrawn from zone 4 through line 8 and, in one specific embodiment of the invention, is directed into separation zone 9. Separation zone 9 may likewise be of any suitable form in order to effect the separation of the gasoline introduced thereto into light and heavy fractions. The light gasoline fraction will usually have an end-boiling point within the range of from about 175° to about 225° F. and the heavy fraction will contain material boiling above this range. The heavy fraction may have an end-boiling point within the range of from 300° to 350° F. more or less.

The light fraction is withdrawn from zone 9 through line 10 and is directed through line 11 into deolefination zone 12. The term "deolefination" as used in the present specification and claims is intended broadly to define the process heretofore described; namely, the reaction or, more accurately, the series of reactions which occur in forming a liquid product, a substantial portion of which boils within the range of the unsaturated gasolines supplied as charging stocks to zones 12 and 20 and has a bromine number substantially lower than that of said charging stocks.

Zone 12 may comprise any suitable apparatus whereby the material introduced thereto may be intimately contacted with the catalyst under the desired conditions of operation. The catalyst may be employed either in the form of granules, pellets, or other preformed shapes, or in the form of finely divided powder. The conditions of operation are, as previously mentioned, from about 400° to about 550° F. and preferably from about 450° to about 500° F. and sufficient pressure to maintain at least a portion of the hydrocarbons in the reaction zone in liquid phase. The pressure employed will usually be within the range of from about 200 to about 1000 pounds, or more, per square inch.

The products from deolefination zone 12 are directed through line 13 into separation zone 14, which likewise may be of any suitable form in order to effect the separation of the products introduced thereto into the desired fractions. In the preferred operation of zone 12, there will be substantially little cracking and therefore almost no gas for separation in zone 14. However, if any gas is formed, the same may be removed by well known means not illustrated. The products in zone 14 are separated into a light gasoline fraction, a heavy gasoline fraction, and any higher boiling material formed during the reaction. The light gasoline fraction is withdrawn from zone 14 through line 15 for blending in a manner to be subsequently described. The material boiling above the range of the desired gasoline product may be withdrawn from zone 14 through line 16 and may be removed from the process, but preferably at least a portion thereof is recycled by way of lines 17 and 1 to zone 2 for further conversion therein.

The heavy gasoline fraction is withdrawn from zone 14 through line 18 and is directed through line 19 into deolefination zone 20. The heavy gasoline fraction previously separated in zone 9 is withdrawn therefrom through line 21 and is preferably directed through line 19 into zone 20 for conversion therein in commingled state with the heavy gasoline fraction withdrawn through line 18 from zone 14.

Deolefination zone 20 will be similar to zone 12 and may employ either the same type or a different type of the catalysts heretofore mentioned. In this case, however, the temperature employed is higher than that utilized in zone 21, and the temperature in zone 20 may thus be within the range of from about 480° to about 700° F. and preferably is within the range of from about 500° to about 600° F. Sufficient pressure is preferably utilized to maintain at least a portion of the hydrocarbons in the reaction zone in liquid phase, and this pressure may, in general, range from about 400 to about 1000 pounds per square inch or more.

The products from zone 20 are directed through line 22 into separation zone 23. Zone 23 may be similar to the previously described separation zones and should be of suitable form to effect the desired separation of the products, which in this case will comprise the separation of a gasoline fraction having the desired end-boiling point from higher boiling material. The gasoline having the desired end-boiling point is withdrawn from zone 23 through line 24 and is commingled with the light gasoline fraction previously separated in zone 14 and withdrawn therefrom through line 15. This material has a relatively high initial octane number and now has a reduced bromine number and improved lead susceptibility so that, upon the addition of the required amount of tetraethyl lead, a final product is obtained which is particularly suitable for use in aviation fuel.

The higher boiling products separated in zone 23 may be withdrawn therefrom through line 25 and may be removed from the process, but preferably at least a portion thereof is directed through lines 26 and 1 to zone 2 for further conversion therein.

The heretofore described specific embodiment of the invention is an operation in which the cracked gasoline is separated into light and heavy fractions prior to the deolefination treatment. The following description covers a process in which the cracked gasoline is subjected to deolefination treatment and the resultant products are fractionated into light and heavy gasoline fractions. The heavy gasoline fraction is then subjected to a separate deolefination treatment at a higher temperature than that employed in the first deolefination treatment.

Referring to the drawing, this operation may be accomplished by directing cracked gasoline of the desired boiling range, which ordinarily will have the usual initial-boiling point and an end-boiling point within the range of about 300° to about 350° F., from line 8 to line 11 into deolefination zone 12, thus bypassing separation zone 9 which may be eliminated in this embodiment of the invention. Zone 12 will be similar to that previously described and will usually employ a temperature within the range of about 400° to about 550° F. under sufficient pressure to maintain at least a portion of the hydrocarbons in the reaction zone in liquid phase. The resultant products are then directed through line 13 into separation zone 14 wherein the desired separation, as heretofore described, is effected. The light gasoline fraction is withdrawn from zone 14 through line 15, while the heavy gasoline fraction is directed through lines 18 and 19 into deolefination zone 20 for treatment in the manner heretofore described, which will be a temperature higher than that employed in zone 12 and thus will be within the range of about 480° to about 700° F. and preferably under sufficient pressure to maintain at least a portion of the hydrocarbons in the reaction zone in liquid phase. The resultant products are directed through line 22 into zone 23, and gasoline fractions having the desired end point, which usually will be within the range of about 300° to about 350° F., are withdrawn therefrom through line 24 for blending with the light gasoline fraction previously separated in zone 14 and withdrawn therefrom through line 15. The higher boiling material withdrawn through lines 16 and 25 from zones 14 and 23 may be removed from the process but preferably is recycled, at least in part, to zone 2 in the manner heretofore described.

As heretofore mentioned, either the same type or a different type of catalyst may be employed in zones 12 and 20. If different type catalysts are employed in these zones, one suitable operation is to utilize the phosphoric acid type catalyst in zone 12 and to utilize the silica base catalyst in zone 20. It is believed that this type of operation will have particular advantage in connection with certain types of gasolines.

Example I

Gas oil is catalytically cracked in a fluidized operation in the presence of a silica-alumina type catalyst at a temperature of 952° F. The catalytically cracked gasoline is separated into two fractions having the following characteristics:

	Light fraction	Heavy fraction
A. P. I. gravity at 60° F.	75.2	43.3
Engler distillation:		
Initial point, °F.	108	210
10%	120	227
50%	135	245
90%	161	277
End point	191	301
Bromine number	96	43
Percent by volume of 300° F.: End point	51	49

The above light gasoline fraction is treated with a catalyst comprising phosphoric acid on a solid support at a temperature of 482° F. and 800 pounds per square inch to yield 66% of gasoline boiling below 200° F. and having a bromine number of 21. The above heavy gasoline fraction is treated with a similar catalyst at a temperature of 563° F. to yield 81% of gasoline boiling below 300° F. and having a bromine number of 20. The residual material boiling below 400° F. is recovered for use in motor fuel, while the residual material boiling above 400° F is recycled to the cracking zone for further conversion therein.

Upon blending of the gasoline fractions boiling below 300° F., a final product of satisfactory bromine number and satisfactory lead susceptibility is obtained, which product is suitable for use in aviation gasoline.

Example II

A catalytically cracked gasoline having a 300° F. end point is treated with a silica-alumina-zirconia catalyst at a temperature of 530° F. under 800 pounds per square inch, and the products thereof are separated into a light gasoline fraction, a heavy gasoline fraction and higher boiling products. The higher boiling products are recycled to the cracking step, while the heavy gasoline fraction is subjected to a separate treatment with a similar type catalyst at a temperature of 620° F. and under a pressure of 800 pounds per square inch. The resultant products are sepa-

rated into gasoline fractions having an end point of 300° F. and higher boiling products. The higher boiling products are recycled to the cracking zone, while the 300° F. end point gasoline is blended with the previously separated light gasoline fraction to produce a final product of satisfactory bromine number and satisfactory lead susceptibility which is suitable for use in aviation fuel.

We claim as our invention:

1. A process for reducing the bromine number of olefinic gasoline which comprises separating the gasoline into a light fraction and a heavy fraction, subjecting said light fraction to the action of a phosphoric acid catalyst at a diolefination temperature of from about 400° F. to about 550° F., subjecting said heavy fraction to the action of a catalyst comprising silica and a refractory oxide at a higher diolefination temperature than the light fraction, and blending gasoline boiling products of the last-mentioned step with gasoline boiling products of the catalytic treatment of said light fraction.

2. The process as defined in claim 1 further characterized in that the first mentioned catalyst comprises ortho phosphoric acid.

3. The process as defined in claim 1 further characterized in that the first mentioned catalyst comprises pyro-phosphoric acid.

4. The process as defined in claim 1 further characterized in that said refractory oxide comprises alumina.

5. The process as defined in claim 1 further characterized in that said refractory oxide comprises zirconia.

6. The process as defined in claim 1 further characterized in that said heavy fraction is subjected to the action of the second-mentioned catalyst at a temperature of from about 480° F. to about 700° F.

7. A hydrocarbon conversion process which comprises subjecting an olefinic distillate boiling in the gasoline range to the action of a phosphoric acid catalyst at a deolefination temperature of from about 400° F. to about 550° F., separating the resultant products into a light gasoline fraction and heavier hydrocarbons, subjecting at least a portion of said heavier hydrocarbons to the action of a catalyst comprising silica and a refractory oxide at a temperature higher than that employed in the treatment of said distillate, and blending gasoline boiling products of the last-mentioned step with at least a portion of said light gasoline fraction.

8. The process as defined in claim 7 further characterized in that said olefinic distillate has an end boiling point below about 350° F.

9. The process as defined in claim 1 further characaterized in that the products of the first-mentioned catalytic treatment are separated into light gasoline and heavier hydrocarbons and at least a portion of the latter supplied to the second-mentioned catalytic treatment.

VLADIMIR HAENSEL.
VLADIMIR N. IPATIEFF.