Sept. 3, 1946. W. A. BAILEY, JR ET AL 2,407,052

GASOLINE AND PROCESS FOR THE PRODUCTION THEREOF

Filed Jan. 30, 1943 3 Sheets-Sheet 1

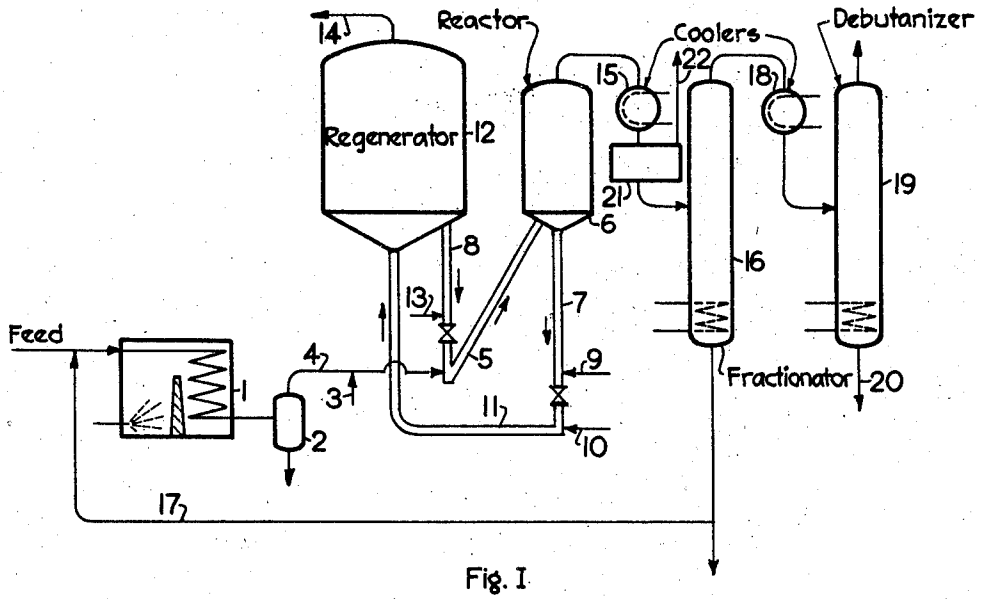


Fig. I

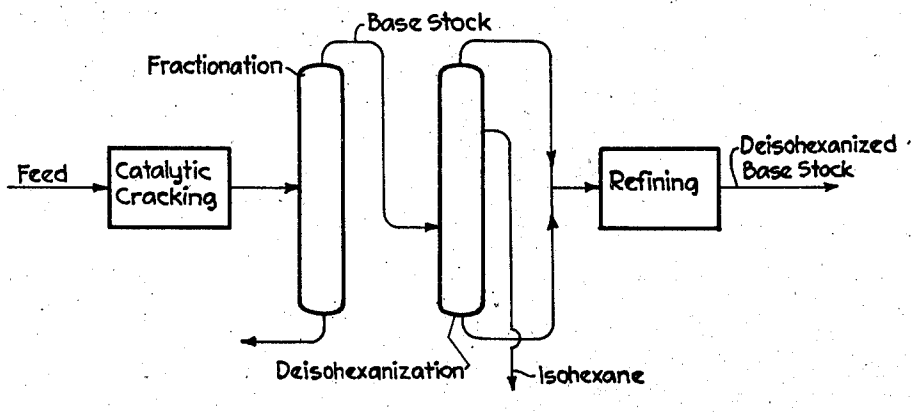


Fig. II

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GASOLINE AND PROCESS FOR THE PRODUCTION THEREOF

Filed Jan. 30, 1943 3 Sheets-Sheet 2

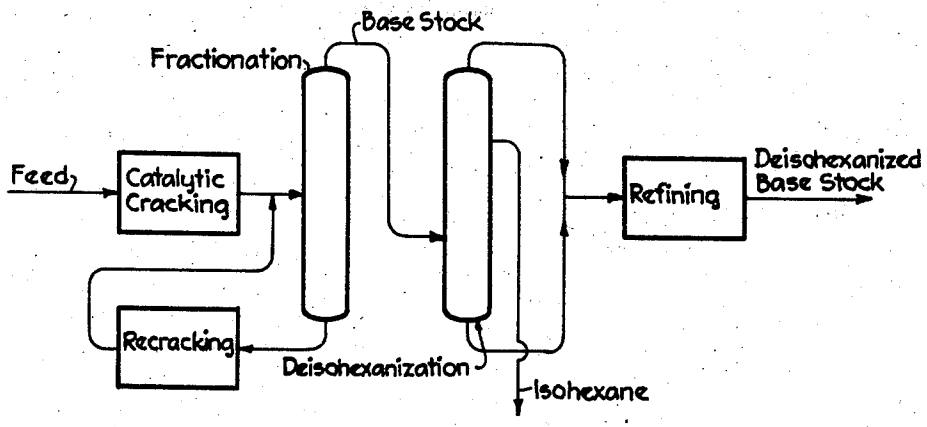


Fig. III

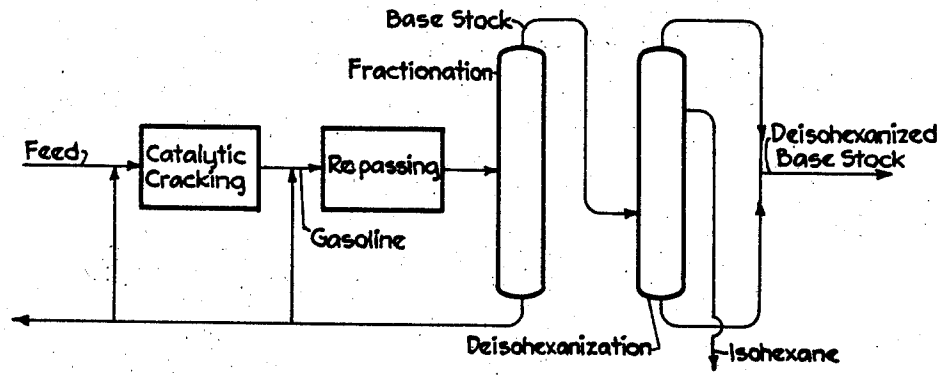


Fig. IV

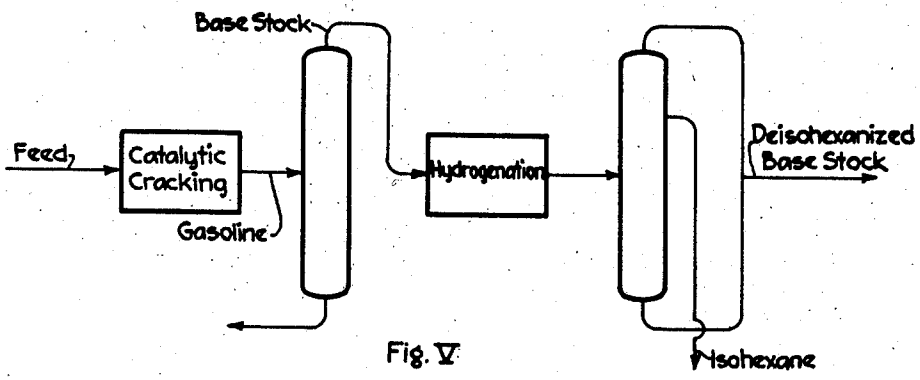


Fig. V

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GASOLINE AND PROCESS FOR THE PRODUCTION THEREOF

Filed Jan. 30, 1943 3 Sheets-Sheet 3

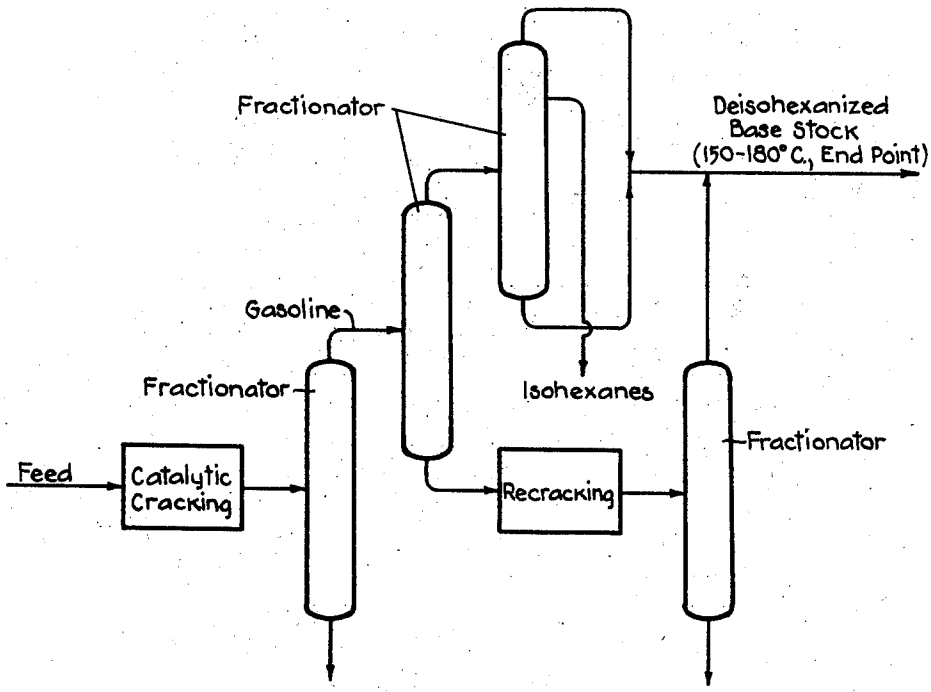


Fig. VI

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UNITED STATES PATENT OFFICE

2,407,052

GASOLINE AND PROCESS FOR THE PRODUCTION THEREOF

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Application January 30, 1943, Serial No. 474,158

7 Claims. (Cl. 196—52)

1

This invention relates to new and improved gasolines and gasoline blending stocks having high performance characteristics in supercharged engines. The invention furthermore relates to a process for the production of said new and improved gasolines and gasoline blending stocks.

An object of the invention is to provide new and improved gasolines and gasoline blending stocks having superior performance characteristics in supercharged engines. A further object of the invention is to provide a process for the economical production of said improved gasolines and gasoline blending stocks. A still further object of the invention is to provide a process whereby gasolines meeting the requirements for supercharged engines may be produced in greater quantity per unit of plant capacity. Other objects of the invention will be apparent in the following disclosure.

The gradual increase in the compression ratios of gasoline engines and the gradual change in gasoline-type fuels to allow efficient operation in the engines employing high compression ratios is common knowledge. This gradual increase in the anti-knock characteristics of gasolines to meet ever increasing engine requirements has been made possible largely by developments along two lines. One is the development of new and improved addition agents such as aniline, toluidine, tetraethyl lead, alkylate, cumene, etc., and the other is in the development of improved base stocks with which the addition agents are blended to give the superior finished fuels. The present invention is a development belonging to the second category.

The various blending agents are in themselves unsuitable as fuels for general use due to their high cost, the limited quantities available, and their volatility characteristics. In order to meet the large demand for high quality fuels it is therefore necessary that these materials be blended with suitable base stocks. The properties most desired in base stocks are high anti-knock rating, suitable volatility, high lead susceptibility, high blending value, and low acid heat value. The branched chain paraffin hydrocarbons generally fulfill most of these requirements and have generally been looked upon as very desirable components in base stocks. Considerable attention has therefore been given to the production of base stocks by the catalytic isomerization of gasoline fractions consisting largely of the normal paraffins. Particular attention has been given to the isomerization of the C_5—C_8 fractions of paraffinic straight run gasoline with aluminum

2

chloride. The various aromatic hydrocarbons also fulfill most of the above requirements. Considerable attention has therefore also been given to the production of highly aromatic base stocks by severe reforming and catalytic dehydrogenation processes. These treatments are, however, only suitable with selected stocks and are quite costly. Furthermore, the aromatic hydrocarbons, although superior to the branched chain paraffin hydrocarbons in certain respects, lack the desired volatility.

It has been found that excellent base stocks which are superior to those produced by either of the above methods may be produced by the catalytic cracking of hydrocarbon oils. In these processes a suitable hydrocarbon oil such as gas oil is catalytically cracked with a clay-type cracking catalyst and a suitable fraction, boiling for instance up to about 150° C., is separated from the product. This material fulfills most of the requirements for high quality aviation base stock, although it is usually somewhat olefinic. It is, however, greatly improved by subjecting it to a repassing treatment and this treatment is therefore frequently applied. The repassing treatment consists essentially in treating the fraction a second time with the same catalyst (or a catalyst of the same type) at a somewhat lower temperature. In the repassing operation straight chain olefins are isomerized to branched chain olefins and the branched chain olefins are hydrogenated to the corresponding branched chain paraffins (apparently by hydrogen exchange reactions) which, in general, have higher anti-knock ratings and higher lead susceptibilities. Other reactions including a small amount of cracking also take place. The base stocks, produced by the described method involving catalytic cracking and repassing, are essentially saturated and comprise large proportions (at least 25% by volume) of aromatic hydrocarbons as well as branched chain paraffin hydrocarbons.

It has now been found that these base stocks may be greatly improved if the isohexanes (i. e. 2-methyl pentane and 3-methyl pentane) which are present in considerable concentrations are substantially removed. Furthermore, it is found that by substantially removing the isohexanes and subjecting the cracked stock to a suitable refining treatment base stocks of equivalent quality may be produced without the necessity of the repassing operation. Furthermore, it has been found that by utilizing the above procedure and repassing only a portion of the catalytically cracked material, increased yields of quality base

stock may be produced. The invention therefore relates to new and improved base stocks, and particularly aviation base stocks, consisting essentially of catalytically cracked gasoline stocks and gasoline stocks of similar character from which isohexanes have been substantially removed, to methods for the preparation of these stocks, and to gasolines having high rich mixture supercharged ratings containing these base stocks.

The base stocks of the invention may be produced by a number of combinations of steps. According to one embodiment of the invention, improved base stocks are produced by catalytically cracking a hydrocarbon oil, separating a lower boiling cracked fraction having the desired final boiling point of the base stock, and fractionating said lower boiling fraction to remove a relatively narrow boiling fraction rich in isohexanes. This modification is illustrated diagrammatically in Figure II of the attached drawings.

The catalytic cracking is effected with a clay-type cracking catalyst such as used in the well-known Houdry cracking process and the competitive cracking processes of this general type. The catalysts used in these processes comprise certain selected neutral clays and earths, modified clays, and synthetic clay-type catalysts. The natural clays are sometimes used in their natural state but are usually treated and/or modified, for instance, by acid washing, removing iron-bearing impurities, leaching out alumina, adjusting the ratio of silica to alumina, and/ or by incorporating minor amounts of promoters in order to increase their activity, stability, etc. and to reduce their carbon-forming tendency. The various synthetic clay-type cracking catalysts are, however, generally superior to the natural clays and modified clays, and are generally preferred. These catalysts usually consist largely of silica and/or alumina and are often modified by minor amounts of such materials are B_2O_3, AlF_3, $AlPO_4$, ZrO_2, MgF_2, MgO, ThO_2, BeO, CeO_2, etc. In some cases, promoting materials such as hydrogen halides, alkyl halides, boric acid vapors, alkyl borates and the like are sometimes added in relatively small concentrations with the feed.

The cracking catalysts of the above-described class, referred to herein as clay-type cracking catalysts, give cracked products which have desirable characteristics and are quite different in composition from the products obtained from other types of cracking processes. In general, the cracked products obtained with the various clay-type cracking catalysts presently employed are relatively rich in branched chain paraffin and in aromatic hydrocarbons. They therefore have, in general, high lead susceptibilities, high blending values, and high anti-knock ratings.

The catalytic cracking step may be carried out with clay-type cracking catalysts in any of a variety of conventional manners. Thus, for example, the cracking may take place in the liquid phase, in the vapor phase, or in the mixed phase. In liquid phase operation the catalyst may be disposed in fixed or moving beds and the oil to be cracked contacted therein under cracking conditions, or the catalyst in a finely divided state may be suspended in the oil and the mixture subjected to cracking conditions in a chamber, coil, or the like. The catalytic cracking step is, however, very advantageously carried out in the vapor phase. In the vapor phase process the catalyst may be disposed in a fixed bed in a suitable converter or catalyst case as in the Houdry process, or in a moving bed as in the Thermofor process (see World Petroleum, 12th Annual Refinery Issue (1942), pages 84–86), or the catalyst in a finely divided state may be contacted with the vapors of the oil to be cracked in one of the so-called dust catalyst processes (see World Petroleum, 12th Annual Refinery Issue, pages 52–55). A particularly advantageous method for effecting the catalytic cracking step is by one of the so-called fluidized catalyst systems of operation in which vapors of an oil to be cracked are "bubbled" up through a body of the finely divided catalyst maintained in an aerated (fluidized) state. One advantageous system utilizing this principle of operation is illustrated diagrammatically in Figure I of the attached drawings. Referring to Figure I, the oil to be cracked is vaporized in a suitable heater 1. Any unvaporized material is separated from the vapors in a separator 2. The preheated vapors in admixture with a small amount of steam and/or inert gas and/or promoting substances introduced via line 3 pass via lines 4 and 5 to converter 6 containing a body of finely divided clay-type cracking catalyst in a fluidized condition. Particularly suitable catalysts for this type of operation are, for example, the so-called silica-alumina composites and boric oxide supported upon active alumina. The conditions in reactor 6 depend upon the particular feed, the particular catalyst, etc., and are adjusted in the conventional manner to give a substantial degree of cracking to produce products boiling in the gasoline boiling range. During the process a portion of the fluidized catalyst is continuously withdrawn via line 7 and an equivalent quantity of freshly regenerated catalyst is picked up from line 8 and carried to the reactor with the feed via line 5. A flushing gas, such as steam, is introduced into line 7 via line 9 to prevent the catalyst from plugging the line and to strip it of a larger part of occluded volatile hydrocarbons. The catalyst withdrawn via line 7 is picked up by a stream of oxygen-containing gas, such as air or a mixture of air and flue gas, entering via line 10 and is carried via line 11 to a regenerator 12 wherein the carbonaceous deposits on the catalyst are burnt off. The freshly regenerated catalyst is withdrawn from the regenerator 12 via line 8. A small amount of inert gas, such as flue gas, air or steam, is introduced into the lower part of line 8 via line 13 to maintain the catalyst in a fluidized condition. The spent regeneration gas is withdrawn via line 14. The hydrocarbon vapors containing the cracked products pass through a cooler 15 to a separator 21. Propane and lighter gases are withdrawn via line 22. The liquid product passes to a fractionator 16 wherein it is separated into a gasoline fraction and a higher boiling fraction. The higher boiling fraction may be recycled in whole or in part, for instance, by means of line 17. The gasoline fraction is usually passed to a cooler 18 and then to a debutanizer column 19. The debutanized gasoline is removed via line 20.

The dust catalyst systems of operation such, for instance, as the fluid catalyst system briefly described above are particularly advantageous in the process of the invention since they produce products generally having superior properties. This is due to the fact that in such systems of operation the catalyst is employed for very short periods between regenerations. When employing processes wherein the catalyst is disposed in fixed beds it is advantageous to employ so-called short cycle operation since the products from such

treatments more nearly approach in quality those obtained in fluidized catalyst operations.

According to the process of the invention, the improved base stocks may be produced from any hydrocarbon oil amenable to catalytic cracking of the described type. In vapor phase cracking operations it is advantageous to treat relatively clean vaporizable hydrocarbon oils such as so-called second cut naphtha, kerosene, gas oil, stove oil, and the like. In such cases where it is desired to avoid a refining or finishing treatment the hydrocarbon feed is preferably relatively free of sulfur. As will be shown, however, high sulfur stocks may also be advantageously treated provided a suitable refining or finishing treatment, such as a sulfuric acid treatment or a hydrofining treatment, is employed.

Referring to Figure II of the drawings, the product obtained from the catalytic cracking step of the process is fractionated to separate a base stock fraction and a heavier fraction which may be recycled, partially recycled, or returned to the refinery for other uses. The final boiling point of the base stock depends upon the type of fuel for which it is to be used, the current allowable end point for the particular type of fuel, the quality of the material, etc., and cannot be definitely fixed. For base stocks for aviation fuels for military use, the present practice is to cut the end point between about 150° C. and 180° C. This may, however, be varied considerably as requirements change. The base stock fraction is carefully fractionated to remove a substantial part of the isohexanes which are normally present in considerable concentrations. The isohexanes, i. e. 2-methyl pentane and 3-methyl pentane, boil at 60° C. and 63° C., respectively. Theoretically, therefore, a fraction boiling between 60° C. and 63° C. would include all of the isohexanes. Actually, however, it is impossible to obtain an absolutely clean-cut separation and a fraction of somewhat broader boiling range is therefore removed. Thus, for example, in commercial practice the lower cut point may be advantageously chosen between about 40° C. and 60° C., and the upper cut point may be advantageously chosen between about 66° C. and 70° C., depending upon the efficiency of the fractionating apparatus. While a very efficient fractionation is not essential, a relatively efficient fractionation is advantageous since it allows more complete separation of the isohexanes and the removal of a smaller fraction of the base stock, and therefore allows greater overall yields of a superior product. Thus, in the preferred practice the fraction removed consists predominantly of isohexanes. In the present conventional practice it is customary to depentanize the base stock, fractionate the pentane fraction to separate isopentane from normal pentane, and reblend the isopentane back with the base stock. This may also be done in preparing the base stocks of the invention. Thus, for example, in a modification of the present process it is advantageous to remove the pentanes and isohexanes in a single fraction. This fraction may then be refractionated to recover the isopentane, and the isopentane may be reblended with the base stock.

The deisohexanized base stock having the desired boiling range may be of suitable quality but often requires a refining treatment. Any of the conventional refining treatments such as those applied to finish gasolines may be employed. A very advantageous treatment, for example, is with sulfuric acid. After such a treatment the material may be caustic washed, dried, and, if desired, refractionated to remove any higher boiling polymers formed in the refining treatment. The refining treatment may be applied to the gasoline fraction either before or after cutting the base stock to the desired end point and either before or after the deisohexanization. If the refining treatment is carried out prior to cutting to the desired end point, a final fractionation of the deisohexanized base stock is not necessary. Another refining treatment advantageously used, particularly when the hydrocarbon treated is relatively high in sulfur, is one of the conventional hydrofining treatments. In these treatments the base stock is subjected to a mild hydrogenation treatment preferably in the vapor phase with one of the various hydrogenation catalysts which are not adversely affected by sulfur compounds under hydrogenation conditions, i. e. sulf-active catalysts such as molybdenum oxide, chromium oxide, zinc oxide, magnesium oxide, nickel sulfide, molybdenum sulfide, tungsten sulfide, copper chromite, heavy metal molybdates and tungstates, heavy metal thio molybdates and thio tungstates, and the like, and combinations thereof. The primary functions of such treatments are to selectively hydrogenate olefinic hydrocarbons and sulfur compounds. In general, any treatment which accomplishes these ends may be employed. As pointed out, in this described modification of the process, superior base stocks are produced without the necessity of the conventional repassing operation. This allows a much greater production capacity for base stock of given quality per unit of reactor space.

In another embodiment of the process of the invention, higher yields of high quality base stock are produced with a somewhat lower but still very high production capacity. According to this modification of the process of the invention illustrated diagrammatically in Figure III of the attached drawings, the cracking step is carried out and the product is fractionated into a gasoline fraction and a higher boiling material which may be recycled in whole or in part, or returned to the refinery for other use, as described above. The end point of the gasoline may advantageously be between about 175° C. and 250° C. The gasoline fraction is then topped to produce a base stock having a desired end point and a heavier gasoline fraction which is recracked under the same or other suitably adjusted conditions. The recracked product is fractionated as before and the base stock is deisohexanized and preferably refined as described above. The recracking of this specific fraction, namely, the gasoline fraction boiling above the base stock range, is particularly advantageous. Thus, for example, in a typical recracking operation on a fraction boiling between 150° C. and 225° C. of a once-through catalytically cracked gasoline, up to about 30% of a substantially saturated material boiling in the base stock range and of high quality may be produced. In this described modification of the process of the invention the production capacity per unit of reactor space is somewhat lower than in the first-described modification, due to the fact that an appreciable amount of material is recracked. The yield of quality base stock, however, is very high due to the additional yields obtained by recracking only the described higher boiling gasoline fraction. In this modification of the process the refining treatment may often be eliminated. A suitable refining treatment, however, generally affords a superior prod-

uct, particularly when the base stock contains appreciable concentrations of sulfur.

According to another modification of the process of the invention, base stocks of much superior properties are produced with approximately the same production capacity and yield per gallon of feed as in the conventional methods. This embodiment of the invention is illustrated diagrammatically in Figure IV of the attached drawings. In this modification of the process the cracking operation is carried out as described and the product is fractionated into a gasoline fraction and a heavier fraction. The gasoline fraction may be cut at any desired end point such, for example, as 175° C. to 225° C. The gasoline fraction or a substantial part of it is then subjected to a conventional repassing treatment. The repassed product is then fractionated to separate a base stock having the desired end point. The heavier gasoline may be recracked or cycled to the repassing treatment, or withdrawn from the system. The repassed base stock of the desired end point is then deisohexanized. The product obtained in this modification of the process is of exceptionally excellent quality and may not require any refining treatment other than the conventional caustic wash.

The repassing operation is effected by contacting material including gasoline of the base stock range with the same catalyst as used in the cracking, or a catalyst of the same type, preferably having good hydrogen-transfer activity, in the same or different apparatus under conditions chosen somewhat milder than used in the catalytic cracking step. For instance, if the catalytic cracking step is carried out at a temperature of 500° C.–540° C. the repassing may be advantageously carried out at about 425° C.–490° C. The conditions in the repassing operation afford transfer of hydrogen from naphthenes to olefins along with a certain amount of cracking, dealkylation and other reactions of complicated nature. Thus, for example, in a typical repassing operation on a once-through catalytically cracked gasoline a substantially saturated base stock of high quality may be produced and if the material to be repassed contains relatively large amounts of gasoline boiling above the base stock range the yield of quality base stock may be increased.

The major factors determining the desirability of various processes for the production of quality base stocks are the production capacity of base stock of given quality per unit of reactor space, the yield of base stock of given quality per barrel of feed, the quality of the base stock obtainable, and the operating cost. The operating costs in the above-described modifications of the process of the invention are all about equal and in some cases somewhat lower than in the conventional methods hitherto employed. On the other hand, the above-described preferred modifications of the process of the invention are superior to the conventional methods hitherto employed in other respects. Thus, other things being equal, the above-described modifications of the process allow production of base stocks of materially improved ignition characteristics, allow materially increased production capacity, and allow increased yields of base stock per barrel of feed.

As pointed out above, the cracked base stocks produced by the catalytic cracking of various hydrocarbon materials with clay-type catalysts in a dust or fluid catalyst system are particularly amenable to the production of the superior base stocks of the invention. When operating the cracking step with a fixed bed, it is advantageous to employ relatively short periods of cracking between successive regenerations of the catalyst. These methods of operation when carried out under suitable conditions yield cracked gasoline fractions which are relatively saturated. The deisohexanization is therefore not made difficult by the presence of large amounts of olefins; also, the base stocks so produced are particularly amenable to a simple sulfuric acid refining treatment and suffer only relatively small losses in such treatment. It is, however, also possible to produce equivalent yields of base stocks of very excellent quality by a modification of the above-described procedure which may be more advantageous and/or economical in certain cases. According to the modification of the process, illustrated in Figure V of the attached drawings, a suitable hydrocarbon material is catalytically cracked with any of the described clay-type cracking catalysts with any of the described systems of operation under conditions chosen to give a relatively olefinic product. Suitable conditions for this type of operation may be established by increasing the cracking temperature, and/or increasing the space velocity, and/or increasing the period between successive regenerations of the catalyst, etc., as is well known in the art. The product is topped and debutanized as described. The olefinic gasoline is then fractionated to separate a base stock of the desired end point having, for example, a bromine number above about 20. The base stock is then deisohexanized in the described manner and subjected to a hydrofining or mild hydrogenation treatment with a sulf-active hydrogenation catalyst as described above to selectively hydrogenate the olefins and part of any sulfur compounds present, and produce a base stock having a desired low acid heat value and sulfur concentration. The base stock may also, if desired, be first hydrogenated and then deisohexanized as described. This method is preferred when it is desired to isomerize the separated isohexane fraction as described below since it produces an isohexane-containing fraction which is free of olefins and therefore more amenable to the isomerization treatment. By this modification of the process and its variants superior base stocks may be produced from high sulfur stocks at a maximum production rate per unit of cracking reactor space and without the necessity of any refining treatment other than a conventional caustic wash. Also, by this modification of the process it is practical to produce larger yields per barrel of feed of superior base stocks of a given supercharged rating since it is found that the final boiling point of the base stock may be increased to include a greater proportion of the cracked gasoline in the base stock. Olefin- and aromatic-containing gasolines produced by thermal methods are per se generally not so amenable to the described hydrogenation and deisohexanization but may be made so by first subjecting them to a conventional isoforming treatment to convert the olefins largely to their branched chain isomers, or to a treatment under conditions such as those described for the repassing operation, in which case saturation of the olefins takes place to a considerable extent simultaneously with their isomerization.

In the modification illustrated in Figure VI, a hydrocarbon oil boiling predominantly above the gasoline boiling range is catalytically cracked with a clay type cracking catalyst. The product

from the catalytic cracking step is separated by fractional distillation into gasoline and a higher boiling fraction. The gasoline is separated by fractional distillation into a higher boiling gasoline fraction and a lower boiling gasoline base stock containing substantial amounts of 2-methylpentane and 3-methylpentane and having a final boiling point within the range of 150° C. and 180° C. The higher boiling gasoline fraction is subjected to a recracking treatment with a clay type cracking catalyst and the product from this recracking treatment is separated by fractional distillation into a gasoline base stock having a final boiling point within the range of 150° C. and 180° C. and a higher boiling gasoline fraction. 2-methylpentane and 3-methylpentane are substantially completely removed from the first-mentioned gasoline base stock by fractionally distilling to separate a fraction consisting predominantly of 2-methylpentane and 3-methylpentane. The gasoline base stock from which the 2-methylpentane and 3-methylpentane have been substantially completely removed is then combined with the gasoline base stock fraction obtained from the recracked product.

While the above-described modifications of the process of the invention allow best yields and production capacity of highest quality base stock at low cost, the principle of the invention may be also applied to other methods wherein substantially saturated base stocks containing large concentrations of isoparaffins are produced.

Very suitable base stocks may also be produced by still another modified process. In this modification naphthenic hydrocarbon oils are subjected to an isomerization treatment or to an isomerization-cracking treatment with an aluminum chloride catalyst, for instance, as described in United States Patent No. 2,266,012. This treatment results not only in the production of large amounts of branched chain paraffin hydrocarbons but also in the isomerization of non-hydroaromatic naphthenes to hydroaromatic naphthenes. The product from the isomerization treatment is then subjected to one of the conventional dehydrogenation or catalytic hydroforming treatments, for instance, such as that described in United States Patent No. 2,288,866. The product from this treatment contains appreciable concentrations of aromatics in addition to the isoparaffins produced in the isomerization treatment. This product is then subjected to the described deisohexanization.

Since the removal of 2-methyl pentane and 3-methyl pentane from gasoline fractions containing appreciable concentrations of these specific hydrocarbons results in a substantial improvement in the properties of the leaded gasoline under rich mixture-supercharge conditions, it will be apparent to those skilled in the art that the principle of the invention may be also applied with more or less advantage in many modifications. In its broader aspect the process of the invention is therefore not restricted to the preferred modifications hereinbefore described.

The isohexane fraction removed from the base stock as described usually consists predominantly of 2-methyl pentane and 3-methyl pentane. These hydrocarbons have A. S. T. M. motor method octane ratings of 73 and 75, respectively. The isohexane fraction may therefore be advantageously blended in ordinary motor fuel or it may be used for any other purpose. Recently, processes have been developed whereby 2-methyl pentane and 3-methyl pentane may be efficiently converted to 2,2-dimethyl butane (neohexane). These processes may be advantageously employed in conjunction with the above modifications of the process of the invention to produce even greater yields of base stock having very high supercharge ratings. Thus, in this modification of the process, the separated isohexane fraction is subjected to a specific isomerization treatment to convert 2-methyl pentane and 3-methyl pentane to 2,2-dimethyl butane and the product or a fraction thereof is blended back with the base stock. The specific details of two suitable methods for carrying out this specific conversion are fully described in copending patent applications Serial Nos. 406,406 and 443,268, filed August 11, 1941, and May 16, 1942, respectively. This results in a very desirable increase in the volatility of the base stock as well as an improvement in the yield and performance under rich mixture-supercharge conditions.

The base stocks prepared as above described may be used in the production of various grades of gasoline for use under various conditions. As pointed out, however, the superiority of the base stocks of the invention is particularly manifest under supercharge conditions. They are therefore primarily intended for use in producing gasoline intended for use in supercharged engines and particularly for the production of fuels of the highest quality obtainable such as desired for aviation gasoline for military use. The superiority of the base stocks of the invention over the base stocks hitherto prepared is more or less proportional to the amount of lead present and is particularly pronounced in highly leaded gasolines. The preferred superior gasolines of the invention therefore contain above 2 cc. and usually 4 cc. of T. E. L. per gallon.

The base stocks of the invention may be used as gasoline per se but are intended to be blended with various blending agents. Any of the conventional blending agents such as isopentane, neohexane, various alkylates, various hydrogenated polymers, cumene, iso-octane, benzene, toluene, etc. may be used. Typical blends producing aviation gasolines having high supercharged ratings are, for example, as follows:

	Blend, percent by volume								
Base stock	35	47.5	50	45	45	53	49	47	50
Isopentane	15	24	15	15	----	17	19	18	10
Neohexane	----	----	----	----	----	----	----	----	5
Butane-butylene alkylate (iso-octane)	50	28.5	25	35	55	30	----	29	----
Hydrogenated hot acid polymerizate octenes (iso-octane)	----	----	----	----	----	----	32	----	25
Cumene	----	----	10	5	----	----	----	6	----
Toluene concentrate	----	----	----	----	----	----	----	----	10

These various blends usually also contain T. E. L. and/or minor amounts (for instance, up to about 2%) of aromatic amines such as aniline, toluidine, xylidine, cymidine, pseudo cumidine, etc. to increase the supercharged rating to at least S+0.5 and usually above S+1. All supercharged ratings herein given refer to the 3C method (more exactly designated method CFR–AFD–3C). Details regarding this method may be obtained from the Aviation Fuel Division of the Cooperative Fuel Research Committee. In the General Army-Navy Aeronautical Specifications for Fuels for Aircraft Engines the method is designated "Method for Supercharged Knock Test" specification AN–BV–F748. Copies of this specification may be obtained upon application to either the Army Air Force Materiel Command, Wright

Field, Dayton, Ohio, or to the Bureau of Aeronautics, Navy Department, Washington, D. C.

The superiority of the present deisohexanized base stocks is illustrated in the following example:

Example I

An East Texas gas oil having the following specifications—

Gravity	° API	34.3
Aniline point	° C	81
Boiling range	° C	266–366

was catalytically cracked in a fluid catalyst system using a finely divided silica-alumina composite catalyst. The conditions were about as follows:

Temperature	° C	470
Pressure	p. s. i. gage	5
Steam diluent	per cent by weight	41

The product was fractionated to separate a debutanized aviation base stock having a final boiling point of about 150° C. When leaded with 4 cc. T. E. L. per gallon, this base stock had a rich mixture supercharged rating equivalent to $S_1+1.0$. This aviation base stock fraction was then deisohexanized by fractional distillation. The deisohexanized base stock when leaded with 4 cc. of T. E. L. per gallon had a rich mixture supercharged rating equivalent to $S_1+2.4$.

The substantial improvement realized by the application of the above described deisohexanized base stocks in gasoline blends such as those given is illustrated in the following example:

Example II

A California second cut straight run naphtha boiling between about 166° C. and 227° C. was catalytically cracked in a fixed bed system using a pilled silica-alumina composite cracking catalyst. The conditions were about as follows:

Temperature	° C	450–500
Pressure		Atmospheric
Liquid hourly space velocity		1
Process period	Minutes	10

The product was debutanized, dependanized and cut to an end point of about 150° C. The base stock was then deisohexanized and blended as follows:

Isopentane	Parts	24
Deisohexanized and dependanized base stock	do	47.5
Butane-butylene alkylate	do	28.5
T. E. L.	cc. per gal.	4

The rich mixture supercharged rating of the blend was equivalent to $S_1+2.9$.

We claim as our invention:

1. A process for the production of base stocks suitable for the production of gasolines having high supercharged ratings which comprises catalytically cracking a hydrocarbon oil boiling predominantly above the gasoline boiling range with a clay-type cracking catalyst, separating the product by fractional distillation into gasoline and a higher boiling fraction, separating said gasoline by fractional distillation into a higher boiling gasoline fraction and a lower boiling gasoline base stock containing substantial amounts of 2-methyl pentane and 3-methyl pentane and having a final boiling point within the range of 150° C. and 180° C., subjecting said higher boiling gasoline fraction to a recracking treatment with a clay-type cracking catalyst, separating the recracked product by fractional distillation into a gasoline base stock having a final boiling point within the range of 150° C. and 180° C. and a higher boiling gasoline fraction, substantially completely removing 2-methyl pentane and 3-methyl pentane from said first gasoline base stock by separating by fractional distillation a fraction consisting predominantly of 2-methyl pentane and 3-methyl pentane, and combining the product with said second gasoline base stock.

2. A process for the production of base stocks suitable for the production of gasolines having higher supercharged ratings which comprises catalytically cracking a hydrocarbon oil boiling predominantly above the gasoline boiling range with a clay-type cracking catalyst, separating the product by fractional distillation into gasoline and a higher boiling fraction, separating said gasoline by fractional distillation into a higher boiling gasoline fraction and a lower boiling gasoline base stock fraction containing substantial amounts of 2-methyl pentane and 3-methyl pentane and having a final boiling point within the range of 150° C. and 180° C., subjecting said higher boiling gasoline fraction to a recracking treatment with a clay-type cracking catalyst, separating the recracked product by fractional distillation into a gasoline base stock fraction having a final boiling point within the range of 150° C. and 180° C. and a higher boiling gasoline fraction, and substantially completely removing 2-methyl pentane and 3-methyl pentane from the combined base stock fractions by separating by fractional distillation a fraction consisting predominantly of 2-methyl pentane and 3-methyl pentane.

3. A process for the production of base stocks suitable for the production of gasolines having higher supercharged ratings which comprises catalytically cracking a hydrocarbon oil boiling predominantly above the gasoline boiling range with a clay-type cracking catalyst, separating the product by fractional distillation into gasoline and a higher boiling fraction, subjecting said gasoline to a recracking treatment with a clay-type cracking catalyst, separating the recracked product by fractional distillation into a higher boiling gasoline fraction and a gasoline base stock containing substantial amounts of 2-methyl pentane and 3-methyl pentane and having a final boiling point within the range of 150° C. and 180° C. and substantially completely removing 2-methyl pentane and 3-methyl pentane from said gasoline base stock by separating by fractional distillation a fraction consisting predominantly of 2-methyl pentane and 3-methyl pentane.

4. A process for the production of base stocks suitable for the production of gasolines having higher supercharged ratings which comprises catalytically cracking a hydrocarbon oil boiling predominantly above the gasoline boiling range in the vapor phase with a cracking catalyst consisting essentially of boric oxide supported upon an active alumina, separating the product by fractional distillation into a higher boiling fraction and a lower boiling gasoline base stock containing substantial amounts of 2-methyl pentane and 3-methyl pentane and having a final boiling point within the range of 150° C. and 180° C., and substantially completely removing 2-methyl pentane and 3-methyl pentane from said gasoline base stock by separating by fractional distillation a fraction consisting predominantly of 2-methyl pentane and 3-methyl pentane.

5. A process for the production of base stocks

suitable for the production of gasolines having higher supercharged ratings which comprises catalytically cracking a hydrocarbon oil boiling predominantly above the gasoline boiling range with a clay-type cracking catalyst in a fluid catalyst cracking system, separating the product by fractional distillation into a higher boiling fraction and a lower boiling gasoline base stock containing substantial amounts of 2-methyl pentane and 3-methyl pentane and having a final boiling point within the range of 150° C. and 180° C., and substantially completely removing 2-methyl pentane and 3-methyl pentane from said gasoline base stock by separating by fractional distillation a fraction consisting predominantly of 2-methyl pentane and 3-methyl pentane.

6. A process for the production of base stocks suitable for the production of gasolines having higher supercharged ratings which comprises catalytically cracking a hydrocarbon oil boiling predominantly above the gasoline boiling range with a silica-alumina cracking catalyst, separating the product by fractional distillation into a higher boiling fraction and a lower boiling gasoline base stock containing substantial amounts of 2-methyl pentane and 3-methyl pentane and

having a final boiling point within the range of 150° C. and 180° C., and substantially completely removing 2-methyl pentane and 3-methyl pentane from said gasoline base stock by separating by fractional distillation a fraction consisting predominantly of 2-methyl pentane and 3-methyl pentane.

7. A process for the production of base stocks suitable for the production of gasolines having higher supercharged ratings which comprises catalytically cracking a hydrocarbon oil boiling predominantly above the gasoline boiling range with a clay-type cracking catalyst, separating the product by fractional distillation into a higher boiling fraction and a lower boiling gasoline base stock containing substantial amounts of 2-methyl pentane and 3-methyl pentane and having a final boiling point within the range of 150° C. and 180° C., and substantially completely removing 2-methyl pentane and 3-methyl pentane from said gasoline base stock by separating by fractional distillation a fraction consisting predominantly of 2-methyl pentane and 3-methyl pentane.

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