

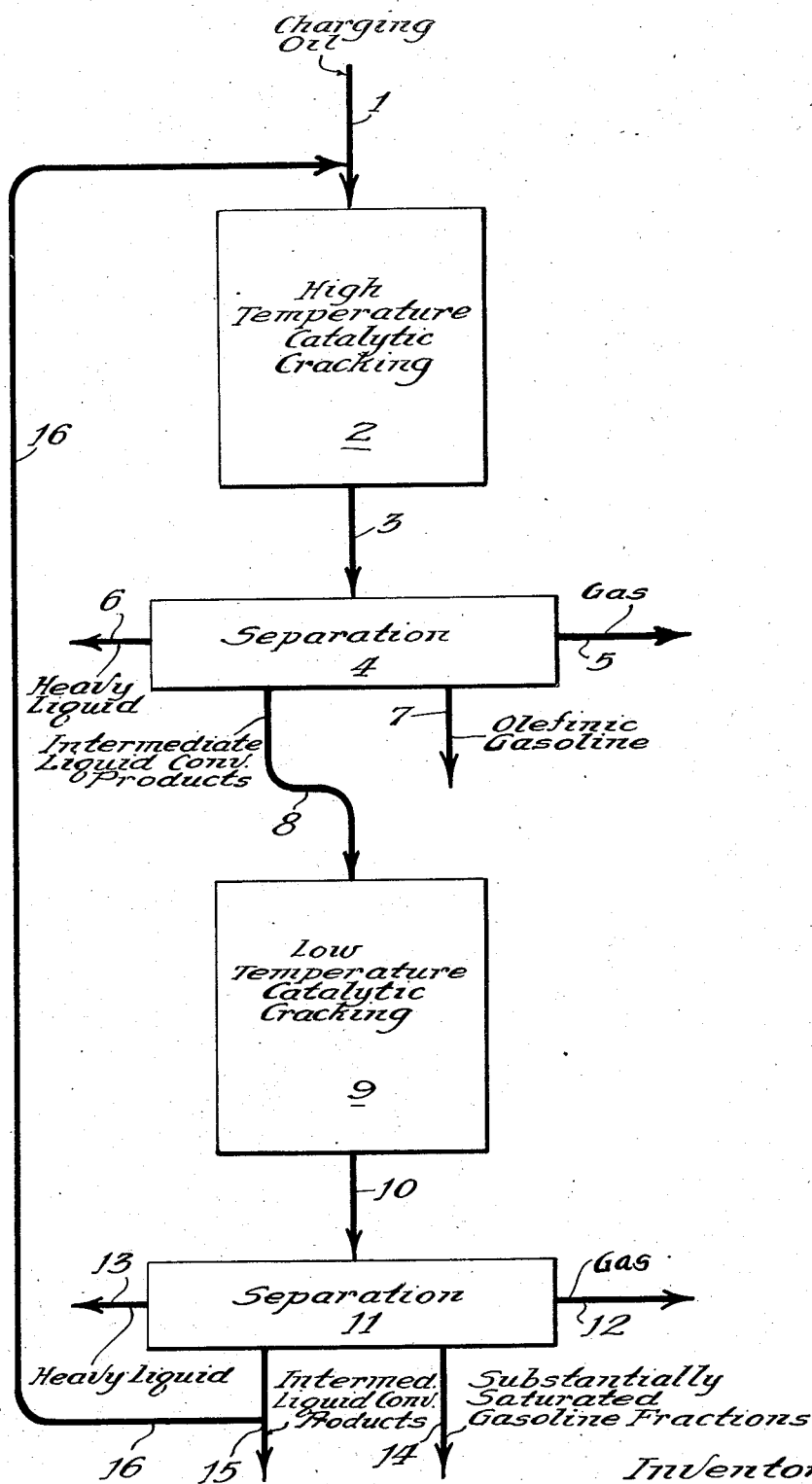
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CATALYTIC CONVERSION OF HYDROCARBONS

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CATALYTIC CONVERSION OF
HYDROCARBONS

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This invention relates to the conversion of hydrocarbon oil to produce large yields of high antiknock gasoline for automotive and aviation purposes. The hydrocarbon oil fractions processed may be from petroleum or from hydrocarbonaceous sources generally, including synthetically produced hydrocarbon mixtures or primary distillates produced in the destructive distillation of hydrocarbon-containing materials such as coals, lignites and shales. The hydrocarbon fractions directed to contact with the catalysts are more usually of a distillate character and are vaporizable without substantial decomposition.

More specifically the invention is concerned with the production of automotive and aviation fuels concurrently from the hydrocarbon oils in thermal-catalytic operations whereby maximum utilization of the hydrocarbons is made in the production of the two fuels. In the first step of the process, automobile blending fuels are made having high antiknock value. Their high antiknock value is apparently due to the highly branched structure of the hydrocarbons present, especially the olefins which constitute the large or major proportion of the product. In the second step of the process the low boiling range product has not only a high antiknock value but also a high content of saturated hydrocarbons. Consequently it has improved properties with respect to storage stability, susceptibility to added antidetonating agents, and blending value, and requires little or no additional refining treatment. The preferred catalysts are characterized by their selectivity in accelerating gasoline-forming rather than gas-forming reactions, by their refractory character which enables them to retain their catalytic properties over long periods of time under commercial conditions of use and regeneration, and by their ease and simplicity of manufacture and their exact reproducibility.

The art of pyrolytically cracking relatively heavy hydrocarbons to produce primarily motor fuel and/or gas is very extensive and it is recognized that most of the basic principles of hydrocarbon decomposition by thermal treatment are known and particular commercial processes have been developed which embody these principles. Where it is desirable to produce motor fuel having octane numbers much above 70, pyrolytic cracking and reforming processes carried out under substantial pressure appear to be limited by the fact that higher antiknock properties are obtained only with decreased yields of gasoline, apparently due to some cracking of the gaso-

line taking place. When catalysts are introduced, however, to modify the conversion reactions, very little is generally known about the specific nature of the hydrocarbon reactions involved and the manner of the catalyst operation, especially where the catalyst has to serve as in commercial practice, for long periods of time under the relatively high temperature conditions of repeated use and regeneration. Due to the complexity of the hydrocarbon conversion reactions and the highly adsorptive character of catalytically active surfaces, even a highly effective catalyst can only be used for a relatively small fraction of its total period of usefulness before it must be regenerated by oxidizing treatment to remove carbonaceous materials. To meet commercial requirements as a cracking catalyst, for example, it must withstand a large number of these regenerations without a large loss in the initial activity. Many substances are described in technical publications and in the patent literature which have catalytic properties in modifying thermal hydrocarbon conversion reactions, but investigation has shown that these substances, practically without exception, while having some measure of the activity required of a commercial catalyst on the initial contact with the hydrocarbons, have little or no activity when carbonaceous materials which normally deposit upon the catalyst in the hydrocarbon conversion reactions are removed by oxidation. The active surfaces are partly or wholly destroyed during the initial contacts or in the initial regeneration treatments so that the prepared substances have academic interest but no commercial value. Even where catalysts have been reported to have commercial possibilities, extreme care has been employed in their use and regeneration in order to retain the initial activity and structural form of the catalyst. The catalysts employed in the present invention are of a rugged character and suitable for prolonged use in commercial practice.

In one specific embodiment the present invention comprises contacting a higher boiling hydrocarbon oil fraction with particles of catalytic material prepared by drying and calcining an alkali metal-free composite of precipitated silica hydrogel with minor amounts of precipitated alumina and zirconia in the primary step of the process at a temperature within the approximate range of 850–1200° F. and at a pressure within the approximate range of atmospheric to 100 pounds per square inch to produce conversion products containing substantial yields

of high antiknock gasoline, separating the conversion products to produce a normally gaseous fraction, said high antiknock gasoline, an intermediate higher boiling fraction, and a high boiling residue fraction to be withdrawn from the process, recovering the high antiknock gasoline containing large proportions of olefinic hydrocarbons as a product of the process, and directing said intermediate higher boiling fraction from the primary step to further catalytic treatment in a secondary step where the hydrocarbon fraction is vaporized and contacted with a similar catalyst as in the first step at a temperature within the approximate range of 500-850° F. and at a pressure of approximately 50 to 1000 pounds per square inch to produce conversion products containing large proportions of a relatively saturated gasoline, separating the conversion products to produce a normally gaseous fraction, said relatively saturated gasoline, and a higher boiling hydrocarbon fraction, recovering the relatively saturated gasoline fraction as a product of the process suitable for use in the manufacture of aviation fuels and returning said higher boiling fraction from the secondary step to further contact with the catalyst in the primary cracking step.

In the primary step where higher temperatures are employed, the space velocities may be within the approximate range of 0.5 to 50, the liquid space velocity being defined as the volume of oil charged hourly per volume of catalyst space in the reactor. Space velocities more generally employed in this step range from approximately 2 to 10. The preferred temperatures more usually range from 900-1000° F. depending in general upon the particular charging stock and the depth of cracking. The gasoline fraction produced usually contains olefinic hydrocarbons of the order of 40-70% or more and has an octane number of approximately 78-80 by the motor method. It cannot be readily treated and converted to a substantially saturated gasoline of the high antiknock value required of aviation fuels. It has, however, an antiknock value higher than that used in fuels for automobile engines at the present time so that it is highly desirable for blending with gasoline fractions of inferior antiknock value to produce automobile fuels of the current market grade.

The normally gaseous fraction separated from the conversion products, especially in the primary step contains a relatively large proportion of olefinic hydrocarbons, particularly C₃ and C₄ olefins which may be advantageously utilized using known polymerization or alkylation processes to obtain further yields of high antiknock gasolines. In these processes, prepared catalysts such as aluminum chloride, phosphoric acid, sulfuric acid, boron fluoride mixed with hydrogen fluoride, etc., may be used. Saturated gasoline hydrocarbons are produced directly by alkylation treatment while with polymerization treatment saturated gasoline may be obtained by the use of additional processing involving hydrogenation.

In the secondary step of the present invention higher boiling hydrocarbons separated from the conversion products of the primary step are more usually processed under non-hydrogenating cracking conditions. Temperatures of 700-800° F. and the liquid space velocities employed may range from approximately 0.5 to 5, the lower space velocities within this range being more generally employed. Although atmospheric and slightly superatmospheric pressure have been

utilized, good results have been obtained at moderate superatmospheric pressures ranging up to 500 pounds per square inch. In some cases even pressures of 1000 pounds per square inch have been employed. The process may be further characterized by the fact that even if hydrogen is present there is no apparent consumption of such hydrogen during conversion. Apart from the operating conditions employed in the secondary step, the degree of saturation of the gasoline product is partly dependent upon the charging stock admitted to the process and the depth of cracking carried out in the primary step. Charging stocks, for example, which are relatively deficient in hydrogen with respect to their aliphatic or cyclic character, or stocks which have been too deeply cracked in the primary step will produce less saturated products in the secondary step. More usually the process of the present invention is carried out so that the two steps are in balance and a maximum over all yield of gasoline is produced in the two steps. It appears that the higher boiling hydrocarbons separated from the gasoline product in the primary step are particularly amenable to catalytic treatment for the formation of relatively saturated gasoline hydrocarbons. Although the olefin content of the gasoline produced in the secondary step is usually sufficiently low for direct use in preparing aviation fuel, the gasoline fraction may be subjected to additional chemical treatment to reduce the olefin content by conventional processes. In any event the relatively saturated gasoline resulting in the secondary step of this process has high storage and color stability, a low copper dish gum content and a relatively low sulfur content since considerable sulfur is eliminated largely as hydrogen sulfide from sulfur-containing oil during the catalytic conversion reactions. Because of these characteristics, the high antiknock value and the high susceptibility to further increase in antiknock value by the addition of tetraethyl lead, this gasoline is especially desirable as an aviation base fuel.

A fraction such as the 300-400° F. cut may be separated from the conversion products of the secondary step and because of its high antiknock value be used for blending purposes in preparing automobile fuels. Higher boiling fractions are preferably returned to the primary step for further catalytic cracking treatment in the production of automobile fuels. In some cases, however, this oil has been relatively highly degraded and may be withdrawn from the process as such or directed to separate cracking treatment for its maximum utilization in motor fuel production under optimum conditions.

The catalyst used both in the primary and secondary steps is preferably of the synthetic type. Although naturally occurring materials such as acid-treated clays including fuller's earth, montmorillonite type clays, some bentonites, etc., may be utilized with or without added activating metal compounds the results are not equivalent to those obtained when using the preferred catalysts which are synthetically prepared in order to produce more highly active and refractory catalysts.

Numerous methods may be employed in preparing the synthetic cracking catalysts which are the subject of the present invention. The components may be separately, concurrently or consecutively precipitated. Generally speaking, the primary and major component is a precipitated hydrated silica which is usually admixed

with a precipitated hydrous metal oxide such as alumina, zirconia, or mixtures thereof present in minor proportions. According to one general method of preparation the hydrated silica may be precipitated from a solution of commercial water glass and subsequently admixed with the remaining hydrous oxide components. The water glass may be diluted to the extent of 8 to 10 times and an acid such as hydrochloric acid added to precipitate the hydrated silica. The concentration and excess acid utilized are regulated so as to obtain optimum precipitating conditions and the hydrated silica may then be filtered to remove the mother liquor. The hydrated silica may then be admixed with the hydrous oxide components in any suitable manner as for example by suspending the precipitated hydrated silica in a solution of salts of the metal components for which the hydrous oxides are desired, and precipitating the hydrous oxide in the presence of the suspended hydrated silica by the addition of an alkaline precipitant, more usually ammonium hydroxide. According to this procedure the precipitated hydrated silica may be slurried in a solution of zirconyl chloride and/or aluminum chloride for example in amounts adequate to produce hydrous oxides in the desired proportions, and ammonium hydroxide added to precipitate said hydrous oxides. Various other procedures may be followed, however, wherein these components may be co-precipitated or separately precipitated to intimately admix the components. The hydrated silica may be heated in solutions of the metal salts and hydrous oxides deposited in the presence of a hydrated silica by hydrolysis, or the precipitated hydrated silica may be admixed with a relatively concentrated solution of the metal salt to form a paste and then heated to deposit the desired metal oxides. The admixed materials are usually dried at ordinary drying temperatures and reduced to a powdered condition for forming into shaped and sized particles. According to other procedures it is possible to extrude the catalytic material while in a wet condition and subsequently dry the moist particles to obtain them in the desired form.

In the manufacture of refractory synthetic catalysts it has been found necessary where sodium compounds have been adsorbed into the catalytic material during preparation to treat the material at some stage of its preparation in order to remove these alkali metal impurities. This may be accomplished according to one procedure by washing the dried composite with acidulated water until the alkali metal impurities have been substantially eliminated. The material is then again dried and formed into particles usually with a lubricant added to facilitate cohesion and prevent adhering or sticking in the briquetting or pilling machines used in forming the material into pills, pellets or other consolidated and shaped particles. Subsequently the formed particles are heated at temperatures of the order of 1000-1500° F. whereby the catalyst assumes a suitable form for prolonged use in the treatment of hydrocarbons. The catalysts are highly porous and possess a large total contact surface. They are not difficult to reactivate by oxidation and retain their high degree of activity during high temperature conditions of alternate use and reactivation for long periods of time.

In both steps of the present invention the catalysts may be conveniently utilized as filling ma-

terial in tubes or chambers in the form of small pellets or granules. The average particle size may vary within the approximate range of 2-10 mesh which may apply to either shaped particles of uniform size such as short, essentially cylindrical shapes, for example, or particles of irregular shape produced by consolidating and sizing the powdered catalytic material. The simple method of preheating the hydrocarbon oil to be processed in each stage to a temperature suitable for conversion in contact with the catalyst, and then passing the vapors over a stationary mass of the catalyst particles may be employed. The preheated vapors may be passed through the catalyst in apparatus where the passage of vapors is restricted to definite paths rather than allowing the vapors to have unrestricted contact with large beds of catalytic material. This facilitates control of the temperature of the contact materials both in processing and during regeneration by using various heat interchange devices and media. Since the commercially useful active period of the preferred catalysts is of relatively short duration before carbonaceous materials deposited thereon have to be removed by oxidation, a plurality of reaction vessels are used in each step so that a continuous operation may be had by regenerating partially spent catalyst out of contact with the stream of hydrocarbon vapors while processing hydrocarbons in contact with the active catalyst. Conversion products removed from both steps of the process are separately fractionated and separated to produce a normally gaseous fraction, the gasoline boiling range fraction and higher boiling hydrocarbons, the major portion of the higher boiling hydrocarbons removed from the primary step being processed in the secondary step and the higher boiling hydrocarbons from the secondary step preferably returned to further cracking treatment in the primary step.

Generally speaking, a suitable aviation base fuel may be produced in the secondary step by varying the conditions of temperature, pressure, space velocity and length of period, these conditions varying more or less with the boiling range and type of hydrocarbons undergoing treatment. More usually additional treatment of the product is not necessary but the process may be operated in such a manner that relatively minor proportions of unsaturated hydrocarbons remaining in the product after processing may be substantially saturated in a hydrogenation step, for example, or removed by well known methods such as acid treatment or solvent refining.

The accompanying drawing is a flow diagram illustrating the process provided by the invention.

Referring to the drawing, the initial charging oil for the process is supplied through line 1 to the high temperature catalytic cracking zone 2 wherein it is catalytically converted in the manner previously described to produce gasoline of relatively high olefin content and higher boiling liquid fractions amenable to further treatment for the production of gasoline low in or substantially devoid of olefins.

There will normally be an incidental production of gas and some heavier liquid conversion products in zone 2 and the resulting fluid products are supplied through line 3 to separation in zone 4, wherefrom gases lighter than or in excess of those desired for inclusion in the olefinic gasoline are discharged through line 5 and wherefrom any heavy liquid products, unsuitable

for the subsequent further treatment provided, are withdrawn through line 6. Gasoline of the desired vapor pressure and boiling range and having a relatively high olefin content is separately removed from separating zone 4 through line 7.

Intermediate liquid conversion products boiling above the range of the gasoline removed through line 7 are directed from separating zone 4 through line 8 to the low temperature catalytic cracking zone 9.

In zone 9 the oil supplied thereto from the initial cracking step is subjected to treatment in the manner previously specified to produce gasoline fractions substantially devoid of olefins or of materially lower olefin content than the gasoline recovered from the initial conversion step. The resulting fluid conversion products are directed from zone 9 through line 10 to separation in zone 11 wherefrom normally gaseous fractions undesired for inclusion in the gasoline product of this step are discharged through line 12. Any heavy residual liquid products may be removed from separating zone 11 through line 13. The gasoline product of the desired vapor pressure and boiling range, which is relatively low and/or substantially devoid of olefins, is directed from separating zone 11 through line 14 to storage or elsewhere as desired. In the preferred embodiment of the invention this product will constitute an aviation base stock of good antiknock value and low bromine number suitable for blending with the other usual ingredients of aviation gasoline to form a product meeting specifications for aviation fuel.

Intermediate liquid conversion products boiling above the range of the product withdrawn through line 14 are removed from the separating zone through line 15 and may be discharged from the system to storage or elsewhere as desired or they may be returned all or in part through line 16 to further catalytic cracking treatment in zone 2 together with the initial charging oil.

The following specific examples are given to illustrate the process of the invention and the type of catalyst preparation preferably utilized. The process should not be considered as limited to these examples of the process or to the particular catalyst preparation, these being given as illustrative of the novelty and utility of the invention.

Example I

In this example the cracking catalyst used in both the primary and secondary steps was a calcined alkali metal-free composite of precipitated silica, alumina and zirconia in the following molal ratio: $100\text{SiO}_2:2\text{Al}_2\text{O}_3:5\text{ZrO}_2$. A commercial water-glass grade of sodium silicate containing approximately 28.5 per cent of silicon dioxide and 9 per cent by weight of sodium oxide was diluted with approximately 10 volumes of water. Hydrochloric acid was added gradually and with constant agitation of the mixture until it was barely alkaline to phenolphthalein. After the silica gel has formed and has been well broken up, a small additional amount of hydrochloric acid was added until the mixture was just acid to Congo red, whereby substantially complete precipitation was effected. The silica gel suspension was then brought back practically to a neutral point when tested with litmus and charged to a filter. The cake on the filter was then removed, broken up and thoroughly agitated and slurried in a solution containing aluminum

and zirconyl chlorides in amounts sufficient to give the desired final composition above noted. Ammonium hydroxide was then added to the slurry until the mixture was just barely acid to litmus after which the material was again filtered. The filter cake was removed and dried to a water content of approximately 20 per cent after which it was ground to pass a 30 mesh screen. The powdered material was washed with acidulated water until the washings gave no further test for sodium using magnesium uranyl acetate reagent. The purified material was then dried, admixed with a lubricant and pilled to form $\frac{1}{8}$ inch cylindrical particles. The pilled particles were calcined at 1500°F . for about one hour to produce the catalytic material in its final active form and stabilize it with respect to subsequent exposure to the high temperatures used in alternate conversion and reactivation steps practiced in the process.

An East Texas gas oil of $30.7^\circ\text{A. P. I. gravity}$ was heated to a temperature of approximately 940°F . and contacted with the above described catalyst disposed in 14-foot beds in a plurality of catalyst tubes. The pressure at the inlet of the tubes was approximately 40 pounds per square inch. The conversion products were fractionated and 21.9% of 400°F . end-point gasoline was obtained having a bromine number of approximately 90. An intermediate boiling stock corresponding to 69.2% of the gas oil charged was separated for processing in the secondary step, and 5.7% by volume of the oil charged of residue was withdrawn from the process. Carbonaceous material to the extent of 0.5% by weight of the charging stock was deposited upon the catalyst and removed by periodic regeneration treatment with oxygen-containing gas. The gasoline produced had a $60.7^\circ\text{A. P. I. gravity}$, a 10.7 Reid vapor pressure and an octane number of 79.7 by the C. F. R. motor method. The intermediate boiling product from the primary step had an A. P. I. gravity of 31.7 and was charged to the secondary step and processed at a temperature of approximately 800°F . and an hourly liquid space velocity of approximately one, using approximately 50 pounds per square inch pressure. As a result of this secondary treatment, approximately 20% by volume of the oil charged was obtained as a 300°F . end-point gasoline having a bromine number of approximately 29 and an octane number of 78 which, upon the addition of 6 cc. of tetraethyl lead per gallon was raised to a 93 octane number. The hydrocarbons boiling above the 300°F . end point motor fuel product was directed back to the primary stage for further treatment in admixture with fresh oil.

Example II

In this example a similar catalyst and similar apparatus was used as in Example I. A Mid-Continent gas oil having a $37.2^\circ\text{A. P. I. gravity}$ was used and was heated to a temperature of approximately 940°F . at a pressure of 45 pounds per square inch. 36% by volume of oil charged of 400°F . end-point gasoline was obtained having a bromine number of 97 and an octane number of 80.5. 45% by volume of the charging stock of a higher boiling intermediate fraction was separated from the conversion products of the primary step and subjected to treatment in the second step of the process at a temperature of approximately 820°F . and a pressure of approximately 100 pounds per square inch to produce 28% by volume of the oil charged of 300°F .

end-point gasoline having a bromine number of 21 and an octane number of 79. Upon the addition of 6 cc. of tetraethyl lead per gallon of gasoline the octane number was raised to 94.

I claim as my invention:

1. A process for producing automotive and aviation fuels which comprises contacting hydrocarbon oil with a cracking catalyst at a cracking temperature adequate to produce olefinic gasoline, separating the latter from the resultant vaporous conversion products and condensing the conversion products heavier than gasoline, subjecting heavier conversion products thus separated to a non-hydrogenating catalytic cracking treatment at lower temperature than employed in the first-mentioned cracking step to produce gasoline of lower olefin content than said olefinic gasoline from said products, and recovering the last-named gasoline thus formed.

2. A process for producing automotive and aviation fuels which comprises contacting hydrocarbon oil with a cracking catalyst at a cracking temperature adequate to produce olefinic gasoline, separating the latter from the resultant vaporous conversion products and condensing the conversion products heavier than gasoline, subjecting heavier conversion products thus separated to a non-hydrogenating catalytic cracking treatment at lower temperature than employed in the first-mentioned cracking step to produce gasoline of lower olefin content than said olefinic gasoline from said products, separating the last-named gasoline from higher boiling hydrocarbons and supplying at least a portion of the latter to the first-mentioned cracking step.

3. The process of claim 1 further characterized in that the cracking catalyst in both conversion steps comprises a calcined composite of silica, alumina and zirconia.

4. The process of claim 1 further characterized in that the cracking catalyst in both conversion steps comprises a calcined composite of silica and alumina.

5. The process of claim 1 further characterized in that the cracking catalyst in both conversion steps comprises a calcined composite of silica and zirconia.

6. A process as set forth in claim 1 wherein the temperature employed in the first-mentioned conversion step is within the range of 850-1200° F., and the pressure employed is within the range of atmospheric to 100 pounds per square inch.

7. A process as set forth in claim 1 where the temperature employed in the second-mentioned conversion step is within the approximate range of 500-850° F., and the pressure employed is within the range of atmospheric to about 1000 pounds per square inch.

8. A process for concurrently producing automotive and aviation fuels from a hydrocarbon oil which comprises subjecting said hydrocarbon oil in admixture with a high boiling fraction from a secondary step hereinafter set forth to contact with a calcined mixture of precipitated hydrated silica and precipitated hydrated alumina, said mixture being substantially free from alkali metal compounds, at a temperature within the approximate range of 850-1200° F., and a pressure within the range of atmospheric to 100 pounds per square inch, fractionating the resultant vaporous conversion products to separate a gaseous fraction, a motor fuel of relatively high olefin content and heavier hydrocarbons boiling above said motor fuel, removing the gaseous fraction

and motor fuel from the process, and subjecting said heavier hydrocarbons boiling above said motor fuel from said primary cracking step to a non-hydrogenating catalytic cracking treatment in the presence of a calcined mixture of precipitated hydrated silica and precipitated hydrated alumina, said mixture being substantially free from alkali metal compounds, at a temperature within the approximate range of 500-850° F., and a pressure within the range of atmospheric to about 1000 pounds per square inch, separating the conversion products into a normally gaseous fraction, an aviation base fuel of relatively low olefin content and a fraction containing hydrocarbons boiling above the aviation base fuel, and returning said high boiling fraction from the secondary step to further treatment in admixture with the charging stock in the primary cracking step.

9. A process for concurrently producing automotive and aviation fuels from a hydrocarbon oil which comprises subjecting said hydrocarbon oil in admixture with a high boiling fraction from a secondary step hereinafter set forth to contact with a calcined mixture of precipitated hydrated oxides of silicon, aluminum and zirconium, said mixture being substantially free from alkali metal compounds, at a temperature within the approximate range of 850-1200° F., and a pressure within the range of atmospheric to 100 pounds per square inch, fractionating the resultant vaporous conversion products to separate a gaseous fraction, a motor fuel of relatively high olefin content and heavier hydrocarbons boiling above said motor fuel, removing the gaseous fraction and motor fuel from the process and subjecting said heavier hydrocarbons boiling above said motor fuel from said primary cracking step to a non-hydrogenating catalytic cracking treatment in the presence of a calcined mixture of precipitated hydrated oxides of silicon, aluminum and zirconium, said mixture being substantially free from alkali metal compounds, at a temperature within the approximate range of 500-850° F., and a pressure within the range of atmospheric to about 1000 pounds per square inch, separating the conversion products into a normally gaseous fraction, an aviation base fuel of relatively low olefin content and a fraction containing hydrocarbons boiling above the aviation base fuel and returning said high boiling fraction from the secondary step to further treatment in admixture with the charging stock in the primary cracking step.

10. A process for concurrently producing automotive and aviation base fuels from a hydrocarbon oil which comprises subjecting said hydrocarbon oil in admixture with oil from a secondary step hereinafter set forth to contact with a cracking catalyst in a primary step under catalytic cracking conditions of temperature and pressure adapted to produce conversion products containing substantial proportions of motor fuel containing relatively high proportions of olefinic hydrocarbons, separating said conversion products to produce a gaseous fraction, said motor fuel of relatively high olefin content, intermediate higher boiling hydrocarbons and a high boiling residue for removal from the process and subjecting said intermediate higher boiling hydrocarbons from the primary cracking step to a non-hydrogenating catalytic cracking treatment in the presence of a cracking catalyst in a secondary cracking step at a lower cracking temperature than that employed in the first mentioned cracking step and adapted to produce

conversion products containing substantial proportions of aviation base fuel of relatively low olefin content, separating said conversion products to produce a gaseous fraction, said aviation base fuel of relatively low olefin content, and a fraction containing hydrocarbons boiling above the aviation base fuel and returning said higher boiling fraction from the secondary step to further treatment in admixture with charging stock in the primary cracking step.

11. A process for producing automotive and aviation fuels which comprises catalytically cracking hydrocarbon oil at a temperature in the approximate range of 850-1200° F. and a liquid space velocity of 0.5 to 50, thereby forming olefinic gasoline, separating the latter from the resultant vaporous conversion products and condensing the conversion products heavier than gasoline, subjecting heavier conversion products thus separated to a non-hydrogenating catalytic cracking treatment at a temperature in the approximate range of 500-850° F. and a liquid space

velocity of about 0.5 to 5 to produce gasoline of lower olefin content than said olefinic gasoline, and recovering the latter.

12. A process for producing automotive and aviation fuels which comprises catalytically cracking hydrocarbon oil at a temperature in the approximate range of 850-1200° F. and a liquid space velocity of 0.5 to 50, thereby forming olefinic gasoline, separating the latter from the resultant vaporous conversion products and condensing the conversion products heavier than gasoline, subjecting heavier conversion products thus separated to a non-hydrogenating catalytic cracking treatment at a temperature in the approximate range of 500-850° F. and a liquid space velocity of about 0.5 to 5 to produce gasoline of lower olefin content than said olefinic gasoline, separating the last-named gasoline from higher boiling hydrocarbons and supplying at least a portion of the latter to the first-mentioned cracking step.

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