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PROCESS FOR HYDROFINING A HIGHLY OLEFINIC GASOLINE

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This invention relates to the treatment of hydrocarbon oils and is more particularly concerned with the treatment of a raw cracked gasoline fraction. The invention is concerned primarily with the treatment of raw cracked gasoline fractions to produce a finished gasoline of commercially acceptable sulfur content, storage stability and octane number.

At the present time it is desirable that commercially acceptable motor gasoline have a sulfur content of not greater than 0.3% by weight and preferably not greater than 0.1%, as measured in accordance with ASTM methods D129–49 and D90–47T. Specifications for commercial motor gasoline likewise require that it pass an "existent gum" test, in accordance with ASTM method D–381, in which the gasoline must show less than 5 mg. of gum per 100 ml. In addition, it is highly desirable that commercial motor gasoline meet the storage stability requirements set forth in ASTM methods D910–48T or D525–49. Finally, the demands of modern high compression engines make necessary the production of motor gasoline possessing a high octane rating, usually determined as "clear research octane number" in accordance with ASTM method D908–48T. Arithmetic averages in January 1952, for motor gasoline sold in 45 U. S. cities indicate research octane ratings of 83.2 and 90.0 for "regular" and "premium" gasolines, respectively, with such gasolines containing an average of 1.35 and 1.75 cc./gal., respectively, of tetraethyl lead.

In modern petroleum refining practice, it is highly advantageous to convert part or all of the higher boiling fractions of the crude oil to materials boiling in the gasoline range. This is effected by processes which involve the "cracking" of the higher boiling hydrocarbons into hydrocarbons boiling in the gasoline range. However, in many cases, the gasoline fraction which is produced by cracking (hereinafter referred to as "raw" gasoline) requires further processing to provide a commercially acceptable product having a sulfur content, storage stability and octane number within the above specified limits. Various processes have been proposed for treating such raw gasoline fractions to bring them within the desired specification limits, and some of these processes have been commercially used with varying effectiveness.

While sulfur compounds are found in varying amounts in petroleum crudes or fractions, the amount of such compounds often exceeds a value corresponding to 1.0% by weight of sulfur. When such a crude or crude fraction is cracked, the raw gasoline product thereby obtained does not meet the above limits with respect to sulfur content. Furthermore, the sulfur compounds in the raw gasoline often exist as thiophenes and compounds of similar cyclic structure. Such cracked raw gasolines are generally of moderate to high octane number, containing 10 to 50% by volume of aromatic hydrocarbons and at least 20% by volume of olefins, and all known methods for removing cyclic sulfur compounds bring about the destruction or conversion of some of these unsaturated hydrocarbons.

For example, when hydrogenation at relatively high pressures and relatively low temperatures is employed, the olefins present in the cracked gasoline are completely hydrogenated to paraffins, i. e.

$$R—CH=CH_2+H_2 \rightarrow R—CH_2—CH_3$$

It is well known that such paraffins have clear research octane numbers which are as much as 40 octane numbers lower than the corresponding olefins from which they were formed. Thus, such treatment of a raw cracked gasoline fraction produces a finished gasoline which is generally of appreciably lower clear research octane number than the raw gasoline, and which is in all cases of lower clear research octane number than would have been obtained if said olefins had not been hydrogenated. Where the cracking operation produces a raw gasoline which satisfies octane number requirements without the addition of tetraethyl lead, e. g., above 83 clear research octane number, such utilization of conventional hydrogenation treatment to remove cyclic sulfur compounds results in a finished gasoline which is of considerably reduced clear octane number and which consequently requires significant quantities of anti-knock additives to achieve octane requirements. Thus, the principal problem which these cracked raw gasoline fractions of high octane number and high sulfur content present is the reduction of sulfur content to commercially acceptable limits without adverse effect upon the clear research octane number. Similarly, when such cracked raw gasoline fractions are relatively unstable, it is necessary to increase their stability to the desired extent without adverse effect upon the other properties of the gasoline. These are problems which have not been solved in a satisfactory and efficient manner by prior processes for treating raw gasoline.

A principal object of the present invention is to provide a process for treating raw gasoline fractions containing at least 20% by volume of olefins and more than 0.1% by weight of sulfur as thiophenic or other cyclic sulfur compounds, which process will eliminate a substantial portion of said sulfur compounds, while maintaining the major portion of said olefins.

It is a further important object to provide a process for treating said raw gasoline fractions, which will eliminate a substantial portion of said sulfur compounds, while increasing or at least maintaining the clear research octane ratings of said raw gasolines.

It is another object of the invention to provide a process of the character indicated which is also effective simultaneously to increase the stability of such raw gasoline fractions.

Still another object is to provide an improved cracked raw gasoline treating process which avoids the shortcomings of treating processes heretofore proposed.

It is a feature of the invention that cracked raw gasoline is treated at an elevated temperature and at a predetermined hydrogen partial pressure in the presence of a material having catalytic activity such that the objectionable cyclic sulfur bodies are converted into readily separable forms, and bodies which render the gasoline unstable are converted to more stable forms, without significantly decreasing the clear research octane number of the raw cracked gasoline, even when the octane number exceeds 80. In many cases, the process of this invention increases the octane number. Thus, the application of the process to raw gasolines of clear research octane number exceeding 80 makes it possible to meet commercial octane requirements without the addition of anti-knock agents.

In accordance with the invention, a cracked raw gasoline fraction containing over 0.1% by weight of sulfur as thiophenes and other cyclic compounds, and containing at least 20% by volume of olefins, is introduced, to-

gether with hydrogen, into a treating zone maintained at a temperature of 825° to 975° F., preferably at a temperature of about 850° to 950° F., in contact with particulate material of the character hereinbelow described. The total pressure in the treating zone and the introduction of hydrogen and raw gasoline are controlled in known manner to provide a hydrogen partial pressure of 20 to 100 p. s. i. (pounds per square inch), preferably 30 to 70 p. s. i. The total pressure of the system may vary over a relatively wide range, but it is generally preferred to use a total pressure not exceeding about 400 p. s. i. g. (pounds per square inch gage).

The particulate contact material employed in the treating zone is alumina of high surface area containing a catalytic promoter comprising a metallic element of group VA, group VIA or group VIII of the periodic table. The alumina of high surface area comprises materials such as activated alumina and similar preparations of high surface area derived from alumina gels. Activated alumina is a commercial product well known in the petroleum treating art and is described, for example, in "Chemical Engineers' Handbook" (John H. Perry, Ed.), third edition (1950), page 905. The particle size of the alumina usable in accordance with the invention may vary over a wide range, e. g., from a fine powder up to about 1 mesh size.

Examples of particularly suitable catalytic promoters comprise molybdenum, chromium, tungsten, cobalt, vanadium, platinum and nickel. Two or more catalytic promoters may be used at the same time; the use of cobalt and molybdenum together, for example, gives excellent results. The promoters are conveniently incorporated with the alumina as oxides or sulfides by known methods of preparation involving impregnation, precipitation or co-precipitation. These oxides or sulfides are partially or completely reduced by hydrogen to their most active form. This reduction may take place in the reaction zone itself or may be effected by preliminary exposure to hydrogen or hydrogen-containing gas. The effective promoter may thus comprise a metallic element of the above-specified groups in the form of an oxide, a sulfide or as the elemental metal.

While substantially pure hydrogen is advantageously used, a gas mixture containing hydrogen and inert gases, such as nitrogen or methane, may be employed with efficacy. In the latter case it is preferable to use a gas mixture having at least about 30% by volume of hydrogen in order to avoid the necessity of passing excessively large amounts of gas through the reaction zone to provide the desired hydrogen partial pressure of 20 to 100 p. s. i. and in order to avoid the necessity of raising the total pressure of the system to a high value.

The term "gasoline fraction" as herein used has its conventional meaning, viz., a hydrocarbon fraction boiling within the temperature range of 90 to 400° F., although it will be apparent that the treating process of this invention is applicable to hydrocarbon fractions in which material boiling within the gasoline range comprises the predominant portion of the fraction.

Cracked raw gasoline fractions from various sources are advantageously treated in accordance with the process of the invention but the improved process is of particular value, as already mentioned, in reducing the sulfur content of cracked raw gasoline fractions of relatively high octane number, e. g., clear research octane numbers of at least about 80, and more particularly between 80 and 90, containing substantial quantities of mono-olefins, such as gasoline fractions produced by the process described and claimed in the copending application of Percival C. Keith, Serial No. 139,758, filed January 20, 1950, now U. S. Patent 2,606,862. As previously mentioned, the present process is effective to remove even large proportions of sulfur bodies, including thiophenes and similar cyclic compounds, without any appreciable adverse affect upon the high octane number of the raw gasoline. In some cases the octane number is essentially unaffected, i. e., it is not changed by more than one or two units, whereas in other cases it is even increased by a substantial extent.

In the process described in the above-mentioned Keith application, a crude hydrocarbon oil, particularly a heavy residual product, is cracked at a temperature of 800 to 1050° F. and at a total pressure of 200 to 800 p. s. i. g. in the presence of a particulate contact material and the regeneration product gases produced by treating spent contact material contaminated with carbonaceous material at a temperature of about 160 to 2500° F. with steam and oxygen of at least 90% by volume purity. The hydrocarbon effluent from that process is fractionated to yield a cracked raw gasoline which may suitably be treated by the process of this invention.

The invention is, however, not limited to cracked raw gasoline fractions produced in any particular manner but is applicable to any cracked raw gasoline having at least 20% by volume of olefins, and thus a clear research octane number greater than that of a virgin naphtha e. g., above about 40. The present process is of particular effectiveness, however, on those cracked raw gasoline fractions having an exceptionally high olefin content, e. g., of the order of 30% by volume higher, and high clear research octane numbers of the order of 80 to 90.

A typical raw gasoline produced by the process of the above-mentioned Keith application has a relatively high octane number, e. g., a clear research octane number of about 90, and contains a high proportion of olefins. Such a raw gasoline generally has, however, a substantial amount of diolefins which tend to render the gasoline unstable as by depositing gums on standing, and when the gasoline has been derived from a crude oil of very high sulfur content, the raw gasoline generally has a substantial quantity of cyclic sulfur compounds such as thiophenes. For example, a Boscan (Venezuelan) crude is characterized by a very high sulfur content of the order of 5% by weight and, when cracked, the resulting raw gasoline will contain about 1.5% by weight or more of sulfur. Thus, although the sulfur content has been reduced, it has not been sufficiently reduced to meet commercial motor gasoline specifications. Cracked raw gasoline fractions to which the present process is of particular application, such as gasoline produced in accordance with the above-mentioned Keith procedure, will generally have the following approximate composition (percent by volume):

0–20% paraffins and naphthenes
25–40% aromatics
30–60% olefins
2–10% diolefins
1–10% sulfur compounds (about 75% thiophenes).

Without tying the invention to any particular theory of operation, the process appears to involve the following types of reactions which take place more or less simultaneously. Thiophenes and related cyclic sulfur compounds are converted to normally gaseous sulfur compounds like hydrogen sulfide, and diolefins are converted to mono-olefins with the formation of some polymeric material. At the same time, aromatic hydrocarbons are not affected and only mild hydrogenation of mono-olefins takes place so that the excellent anti-knock properties of the raw gasoline are not impaired. In addition, dehydrogenation of naphthenes is facilitated by the conditions employed, resulting in the formation of additional quantities of aromatic compounds of excellent anti-knock characteristics.

The raw gasoline treating process is suitably carried out in conventional gasoline treating apparatus wherein, in accordance with the invention, the raw gasoline is introduced into a reaction zone in contact with particulate catalytically promoted alumina. The apparatus shown in the above-mentioned Keith application may be em-

ployed, but preferably the process is carried out in a fluidized bed such as is used commercially in the catalytic cracking of hydrocarbon oils, the hydrogen or hydrogen-containing gas being advantageously employed as the fluidizing medium. The contact material is continuously or intermittently withdrawn from the treating zone and regenerated in any convenient manner, as by treating it at elevated temperature with oxygen or air and, if desired, other gaseous materials such as steam.

The particular apparatus used for the process and the particular method of regenerating the catalyst form no part of the present invention and any convenient apparatus and method of catalyst regeneration may be employed. In regenerating the catalyst care must be taken, however, in accordance with commercial regeneration techniques, to avoid the use of temperatures which destroy or adversely affect the catalyst. In the regeneration of the promoted activated alumina catalyst of the present process, temperatures in excess of 1200° F. are generally to be avoided.

In order to facilitate the maintenance of the desired temperature in the reaction zone, the raw cracked gasoline to be treated is advantageously preheated to a temperature of 400° to 800° F., preferably about 500° to 700° F., before being fed into the reaction zone. At such temperatures the gasoline is at least partially vaporized. The hydrogen or hydrogen-containing gas may also be preheated to about the same temperature as the gasoline.

Treatment of the cracked raw gasoline in the reaction zone under the specified conditions is carried out to an extent sufficient to reduce the sulfur content of the raw gasoline and to improve its stability to the desired degree. Advantageously, the desired reaction is insured by employing a raw gasoline feed rate in the range of 0.5 to 5, preferably 0.5 to 1.5, volumes of liquid per hour per volume of catalyst, while employing a hydrogen flow rate of 500 to 2500 standard cubic feet (calculated as pure hydrogen) per barrel of raw gasoline fed.

The effluent from the treating zone will contain vapors of the hydrocarbons within the gasoline range admixed with a small amount of higher boiling hydrocarbons formed by polymerization and/or condensation in the reaction zone, and with more volatile compounds including readily removable sulfur compounds formed by the breakdown of thiophenes and like refractory sulfur compounds in the reaction zone. The effluent is fractionally distilled to separate the desired gasoline fraction from the other constituents.

The finished gasoline fraction thus produced is of low sulfur content, high stability and high octane number and meets the specifications for commercial motor gasoline notwithstanding the presence of a substantial quantity of sulfur compounds and diolefins originally in the cracked raw gasoline. The sulfur content of the finished gasoline can be reduced to below 0.1% by weight by the present process, as well as below the 0.3% by weight level presently accepted for marketable motor gasoline.

For a further understanding of the invention, reference is made to the following specific examples which are intended as illustrative of the process without, however, being intended as limitative thereof.

In the following examples the cracked raw gasoline which is treated was obtained from heavy Boscan (Venezuelan) crude oil which was subjected to cracking in accordance with the aforesaid Keith process at a temperature of about 900° F. in the presence of the regeneration gases resulting from the decomposition of the carbonaceous residue on the particulate carrier with steam and oxygen of 95% by volume purity at a temperature of about 1700° F. The effluent from the cracking operation was condensed and fractionally distilled to separate the raw gasoline fraction which has the following characteristics:

Total sulfur, wt. percent (ASTM–D129–49)	1.84
Sulfur as thiophenes, wt. percent	1.3
Octane number, CFRR clear (ASTM–D908–48T)	88
Olefin content, vol. percent	45
Copper dish gum, mg./100 ml. (ASTM–D910–48T)	400
Distillation range, °F. (ASTM–D86–46)	102–400

Sulfur as thiophenes, reported herein, was determined by the Bureau of Mines procedure (R. I. 3591, December 1941). The olefin content of the raw cracked gasolines, reported herein, was determined by chromatographic adsorption analysis. However in the following examples, the olefin content of the finished gasoline, from which thiophenes and other interferents have been substantially removed, was determined conventionally by bromine number.

Example 1

This raw gasoline is heated, for example, by passing through the coils of a tube still, to a temperature of about 700° F. which results in the complete vaporization of the gasoline. The gasoline is then discharged into a reaction zone containing fluidized particles of cobalt-molybdenum promoted activated alumina. The catalyst is prepared by suspending alumina gel in a solution of cobalt nitrate, and thereto adding a solution of ammonium molybdate. The precipitate is filtered, carefully washed and dried. The dried solid is calcined at approximately 850° F. and then classified to the desired particle size range for fluidization. The gaseous treating atmosphere is provided and the fluidization of the catalyst particles is effected simultaneously by introducing a stream of hydrogen into the bottom of the reaction zone. A portion of the fluidized catalyst is continuously removed from the reaction zone and passed to a regenerator, and a corresponding amount of regenerated catalyst, with or without treatment with hydrogen, is continuously returned to the reaction zone. In the reaction zone, the temperature is maintained at 875° F. and the total pressure is maintained at 48 p. s. i. g. The heated raw gasoline is introduced into the reaction zone at a rate to provide a space velocity of 0.5 volume of liquid gasoline per hour per volume of catalyst in the reaction zone and the hydrogen is introduced at a rate to provide a hydrogen partial pressure of 48 p. s. i.

The gasiform effluent is continuously removed from the top of the reaction zone, condensed, and then subjected to fractional distillation to separate from the gasoline fraction more volatile compounds and gases, particles of the catalyst which may have been carried over with the effluent, and a small heavy residue composed primarily of polymers and condensation products formed in the reaction zone. Analysis of the recovered gasoline fraction shows it to have the following characteristics:

Total sulfur, wt. percent (ASTM–D129–49)	0.18
Octane number, CFRR Clear (ASTM–D908–48T)	87.5
Bromine number, cg./gm. (ASTM–D875–46)	37
Olefin content, vol. percent	25
Copper dish gum, mg./100 ml. (ASTM–D910–48T)	4.9
Existent gum, mg./100 ml. (ASTM–D381–49)	less than 5

The yield of gasoline is 89.6% by volume of charge, and the total yield of liquid products is 93.7% by volume of charge.

It will be seen from the foregoing example that, in accordance with the process therein described, a cracked raw gasoline having a high content of sulfur as thiophenes and high in gum forming constituents is converted to a finished gasoline containing a substantial quantity of olefins and of low sulfur content meeting commercial requirements. The finished gasoline likewise meets specifications for existent gum and indicates an excellent storage stability as indicated by the very low value obtained in the copper dish gum test. In the foregoing example,

these substantial reductions in sulfur and gum bodies have been effected without any significant lowering of the clear research octane number of the raw cracked gasoline.

Example 2

Following the procedure described in Example 1, another portion of the above-described cracked raw gasoline is treated in a reaction zone maintained at a temperature of 920° F. and a total pressure of 30 p. s. i. g., by introducing the preheated raw gasoline at a rate to provide a space velocity of 1.1 volumes of gasoline per hour per volume of the catalyst, while providing a hydrogen partial pressure of 32 p. s. i.

The treated gasoline fraction, recovered as described in Example 1, has the following characteristics:

Total sulfur, wt. percent (ASTM–D129–49)	0.23
Octane number, CFRR clear (ASTM–D908–48T)	89.6
Bromine number, cg./gm. (ASTM–D875–46)	45
Olefin content, vol. percent	31
Copper dish gum, mg./100 ml. (ASTM–D910–48T)	7
Existent gum, mg./100 ml. (ASTM–D381–49)	4

The yield of gasoline is 87.3% by volume of charge, and the total yield of liquid products is 91.9% by volume of charge.

In this case along with a substantial reduction in sulfur bodies and in gum-forming bodies to commercially acceptable levels, there is an actual increase in the octane number.

Example 3

The maintenance of the temperature and the hydrogen partial pressure in the reaction zone within the prescribed limits is critical in preventing an adverse affect upon the octane number. Thus, in tests in which temperatures lower than, and/or hydrogen partial pressures greater than the specified ranges are employed, drastic reductions in octane number occur. As an illustration of the influence of temperature, the procedure described in Example 1 was repeated employing operating conditions approximating those used in Examples 1 and 2, viz., a total pressure of 45 p. s. i. g., a hydrogen partial pressure of 43 p. s. i. and a space velocity of 1.0 volume per hour per volume, but the temperature was reduced to 826° F. In this case, the treated gasoline fraction was found to have the desired low sulfur and gum contents, but the clear research octane number was reduced to 81.6. This example indicates that further reduction in temperature would markedly impair the quality of the gasoline. The yield of gasoline is 96.7% by volume of charge, and total yield of liquid products is 99.5% by volume of charge.

Example 4

An increase in hydrogen partial pressure above the specified range of this invention was found to completely eliminate the olefins originally present in the raw cracked gasoline, thereby drastically reducing the octane number. In this case, a temperature of 820° F. was employed with a space velocity of 1.0 volume per hour per volume, but the total pressure was 206 p. s. i. g. providing a hydrogen partial pressure of 156 p. s. i. Although the finished gasoline produced in this case satisfied sulfur and gum requirements, it was found to have a bromine number of 2 cg./gm. and a clear research octane number of 66.0. Thus, essentially no olefins were present in the finished gasoline and the octane number had been reduced to an extent necessitating the addition of large quantities of tetraethyl lead or other anti-knock additives to meet commercial octane number requirements.

Example 5

The following example shows the process of the invention as carried out with a catalyst of molybdenum-promoted activated alumina containing silica. The catalyst is prepared by impregnating a silica-stabilized alumina gel with molybdenum nitrate, drying and calcining in the usual manner. The raw gasoline was prepared in the manner above described in connection with the raw gasoline used in Examples 1, 2, and 3, and had the following characteristics:

Total sulfur, wt. percent (ASTM–D129–49)	1.90
Sulfur as thiophenes, wt. percent	1.3
Octane number, CFRR clear (ASTM–D908–48T)	87
Olefin content, vol. percent	45
Copper dish gum, mg./100 ml. (ASTM–D910–48T)	400
Distillation range, °F. (ASTM–D86–46)	122–400

In accordance with the procedure described in Example 1, the raw gasoline is preheated to a temperature of about 700° F. The gasoline is then passed into a reaction zone containing fluidized particles of the catalyst and subjected to treatment at a temperature of 853° F. in an atmosphere of hydrogen introduced into the reaction zone and serving as the fluidizing medium. The catalyst is continuously regenerated as in Example 1. In the reaction zone a total pressure of 75 p. s. i. g. and a hydrogen partial pressure of 70 p. s. i. are maintained, and the preheated raw gasoline is introduced at a rate to produce a space velocity of 0.5 volume of liquid gasoline per hour per volume of catalyst in the reaction zone. The product gasoline fraction, recovered as in Example 1, had the following characteristics:

Total sulfur, wt. percent (ASTM–D129–49)	0.24
Octane number, CFRR clear (ASTM–D908–48T)	86.1
Bromine number, cg./gm. (ASTM–D875–46)	46
Olefin content, vol. percent	32
Copper dish gum, mg./100 ml. (ASTM–D910–48T)	6
Existent gum, mg./100 ml.	Less than 5

The yield of gasoline is 82.6% by volume of charge, and the total yield of liquid products is 88.8% by volume of charge. The sulfur content and the gum characteristics of this product gasoline are within the desired range and the octane number has not been reduced to any significant extent.

Similar results are obtained when the foregoing tests are carried out with a catalyst formed from activated alumina carrying a promoter comprising other metallic elements of groups VA, VIA, and VIII of the periodic table such as vanadium, chromium, tungsten, platinum and nickel. The tungsten, platinum and nickel promoted catalysts are prepared by impregnation of suspended alumina gel with aqueous solutions of salts of these metals, e. g. ammonium tungstate, platinic chloride or nickelic nitrate, whereas the chromium promoted catalyst is similarly prepared using chromic anhydride. The vanadium promoter is added by cooling a hot aqueous solution of ammonium meta-vanadate in which alumina has been suspended. Drying, calcination and sizing of these catalysts is conventionally effected.

In treating raw gasolines under the conditions of this invention, it has been observed that, in addition to removal of sulfur from raw cracked gasoline, the process is effective in removing amines, phenols, and like oxygen and nitrogen compounds which may likewise be present in such raw gasolines.

In view of the various modifications of the invention which will occur to those skilled in the art upon consideration of the foregoing disclosure without departing from the spirit or scope thereof, only such limitations should be imposed as are indicated by the appended claims.

What is claimed is:

1. A method of desulfurizing a highly olefinic hydrocarbon fraction, which comprises bringing hydrogen and a hydrocarbon fraction containing more than 1% by weight of sulfur in the form of cyclic sulfur compounds and a volume of olefins greater than the volume of

paraffins and naphthenes therein, said volume of olefins being more than 20% by volume of said hydrocarbon fraction and imparting to said hydrocarbon fraction a high octane number into contact with an alumina of high surface area containing a catalyst promoter comprising an element selected from the class consisting of the metallic elements of groups VA, VIA and VIII of the periodic table in a reaction zone maintained at a temperature in the range of 825 to 975° F., the contact of said hydrogen and said hydrocarbon fraction resulting in a net consumption of hydrogen, passing said hydrocarbon fraction through the reaction zone at a space velocity in the range of about 0.5 to 5 liquid volumes per hour per volume of said alumina, maintaining the partial pressure of hydrogen in said reaction zone in the range of 20 to 100 p. s. i., and recovering from the resulting reaction effluent a highly olefinic hydrocarbon fraction containing less than 0.3% by weight of sulfur and a major portion of said olefins and having a high octane number.

2. A method of desulfurizing a highly olefinic hydrocarbon fraction, which comprises bringing hydrogen and a hydrocarbon fraction containing more than 0.1% by weight of sulfur in the form of cyclic sulfur compounds and a volume of olefins greater than the volume of paraffins and naphthenes therein, said volume of olefins being more than 30% by volume of said hydrocarbon fraction and imparting to said hydrocarbon fraction a high octane number into contact with an alumina of high surface area containing a catalyst promoter comprising an element selected from the class consisting of the metallic elements of groups VA, VIA and VIII of the periodic table in a reaction zone maintained at a temperature in the range of 850 to 950° F., the contact of said hydrogen and said hydrocarbon fraction resulting in a net consumption of hydrogen, passing said hydrocarbon fraction through the reaction zone at a space velocity in the range of about 0.5 to 5 liquid volumes per hour per volume of said alumina, maintaining the partial pressure of hydrogen in said reaction zone in the range of 20 to 100 p. s. i., and recovering from the resulting reaction effluent a highly olefinic hydrocarbon fraction containing substantially less than 0.1% by weight of sulfur and a major portion of said olefins and having a high octane number.

3. A method of desulfurizing a highly olefinic gasoline fraction, which comprises hydrogen and a gasoline fraction containing more than 1% by weight of sulfur in the form of cyclic sulfur compounds and a volume of olefins greater than the volume of paraffins and naphthenes therein, said volume of olefins being more than 30% by volume of said gasoline fraction which has a clear research octane number of at least about 80 into contact with an alumina of high surface area containing a catalyst promoter comprising an element selected from the class consisting of the metallic elements of groups VA, VIA and VIII of the periodic table in a reaction zone maintained at a temperature in the range of 850 to 950° F., the contact of said hydrogen and said gasoline fraction resulting in a net consumption of hydrogen, passing said gasoline fraction through the reaction zone at a space velocity in the range of about 0.5 to 5 liquid volumes per hour per volume of said alumina, maintaining the partial pressure of hydrogen in said reaction zone in the range of 20 to 100 p. s. i., and recovering from the resulting reaction effluent a highly olefinic gasoline fraction containing less than 0.3% by weight of sulfur and a major portion of said olefins and having a clear research octane number of at least about 80.

4. A method according to claim 3 wherein the catalyst promoter comprises molybdenum and the hydrogen partial pressure is in the range of 30 to 70 p. s. i.

5. A method of desulfurizing a highly olefinic gasoline fraction, which comprises bringing hydrogen and a gasoline fraction containing more than 0.3% by weight of sulfur in the form of cyclic sulfur compounds and a volume of olefins greater than the volume of paraffins and naphthenes therein, said volume of olefins being more than 30% by volume of said gasoline fraction which has a clear research octane number of at least about 80 into contact with an alumina of high surface area containing a catalyst promoter comprising an element selected from the class consisting of the metallic elements of groups VA, VIA and VIII of the periodic table in a reaction zone maintained at a temperature in the range of 850 to 950° F., the contact of said hydrogen and said gasoline fraction resulting in a net consumption of hydrogen, passing said gasoline fraction through the reaction zone at a space velocity in the range of about 0.5 to 5 liquid volumes per hour per volume of said alumina, maintaining the partial pressure of hydrogen in said reaction zone in the range of 20 to 100 p. s. i., and recovering from the resulting reaction effluent a highly olefinic gasoline fraction containing less than 0.3% by weight of sulfur and a major portion of said olefins and having a clear research octane number of at least about 90.

6. A method of desulfurizing a highly olefinic gasoline fraction, which comprises bringing hydrogen and a gasoline fraction containing more than 0.1% by weight of sulfur in the form of cyclic sulfur compounds and a volume of olefins greater than the volume of paraffins and naphthenes therein, said volume of olefins being more than 20% by volume of said gasoline fraction and imparting to said gasoline fraction a high octane number into contact with an alumina of high surface area containing a catalyst promoter comprising an element selected from the class consisting of the metallic elements of groups VA, VIA and VIII of the periodic table in a reaction zone maintained at a temperature in the range of 825 to 975° F., the contact of said hydrogen and said gasoline fraction resulting in a net consumption of hydrogen, passing said gasoline fraction through the reaction zone at a space velocity in the range of about 0.5 to 5 liquid volumes per hour per volume of said alumina, maintaining the partial pressure of hydrogen in said reaction zone in the range of 20 to 100 p. s. i., and recovering from the resulting reaction effluent a highly olefinic gasoline fraction containing substantially less than 0.1% by weight of sulfur and a major portion of said olefins and having a high octane number.

7. A method of desulfurizing a highly olefinic gasoline fraction, which comprises bringing hydrogen and a gasoline fraction containing more than 0.1% by weight of sulfur in the form of cyclic sulfur compounds and a volume of olefins greater than the volume of paraffins and naphthenes therein, said volume of olefins being more than 20% by volume of said gasoline fraction which has a clear research octane number of at least about 80 into contact with an alumina of high surface area containing a catalyst promoter comprising an element selected from the class consisting of the metallic elements of groups VA, VIA and VIII of the periodic table in a reaction zone maintained at a temperature in the range of 850 to 950° F., the contact of said hydrogen and said gasoline fraction resulting in a net consumption of hydrogen, passing said gasoline fraction through the reaction zone at a space velocity in the range of about 0.5 to 5 liquid volumes per hour per volume of said alumina, maintaining the partial pressure of hydrogen in said reaction zone in the range of 30 to 70 p. s. i., and recovering from the resulting reaction effluent a highly olefinic gasoline fraction containing substantially less than 0.1% by weight of sulfur and a major portion of said olefins and having a clear research octane number of at least about 80.

8. A method according to claim 7 wherein the catalyst promoter comprises molybdenum and the gasoline fraction passes through the reaction zone at a space velocity of 0.5 to 1.5 liquid volumes per hour per volume of said alumina.

9. A method of desulfurizing a highly olefinic gasoline

fraction, which comprises bringing hydrogen and a gasoline fraction containing more than 0.1% by weight of sulfur in the form of cyclic sulfur compounds and a volume of olefins greater than the volume of paraffins and naphthenes therein, said volume of olefins being more than 30% by volume of said gasoline fraction which has a clear research octane number of at least about 80 into contact with an alumina of high surface area containing a catalyst promoter comprising an element selected from the class consisting of the metallic elements of groups VA, VIA and VIII of the periodic table in a reaction zone maintained at a temperature in the range of 850 to 950° F., the contact of said hydrogen and said gasoline fraction resulting in a net consumption of hydrogen, passing said gasoline fraction through the reaction zone at a space velocity in the range of about 0.5 to 5 liquid volumes per hour per volume of said alumina, maintaining the partial pressure of hydrogen in said reaction zone in the range of 20 to 100 p. s. i., and recovering from the resulting reaction effluent a highly olefinic gasoline fraction containing substantially less than 0.1% by weight of sulfur and a major portion of said olefins and having a clear research octane number of at least about 90.

10. A method according to claim 9 wherein the catalyst promoter comprises molybdenum and cobalt and the gasoline fraction passes through the reaction zone at a space velocity of 0.5 to 1.5 liquid volumes per hour per volume of said alumina.

11. A method of desulfurizing a highly olefinic gasoline, which comprises bringing hydrogen and a raw gasoline containing an appreciable quantity of troublesome foreign matter of the class of cyclic sulfur compounds and gum-forming bodies and containing a volume of olefins greater than the volume of paraffins and naphthenes therein, said volume of olefins being more than 20% by volume of said raw gasoline, which has a clear research octane number of at least 80, into contact with activated alumina containing a catalyst promoter comprising a metallic element of group VIA of the periodic table in a reaction zone maintained at a temperature in the range of 850 to 950° F., the contact of said hydrogen and said raw gasoline resulting in a net consumption of hydrogen, passing said raw gasoline through the reaction zone at a space velocity in the range of about 0.5 to 5 liquid volumes per hour per volume of said alumina, maintaining the partial pressure of hydrogen in said reaction zone in the range of 20 to 100 p. s i., and recovering from the resulting reaction effluent a highly olefinic finished gasoline substantially free of troublesome foreign matter and containing at least 20% by volume of said olefins and having a clear research octane number over 80.

12. A method according to claim 11 wherein the catalyst promoter comprises cobalt and the hydrogen partial pressure is in the range of 30 to 70 p. s. i.

13. A method according to claim 11 wherein the catalyst promoter comprises molybdenum and the raw gasoline passes through the reaction zone at a space velocity of 0.5 to 1.5 liquid volumes per hour per volume of said alumina.

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