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PROCESS FOR TREATING HYDROCARBONS

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This invention relates to the treatment of hydrocarbons and relates more particularly to catalytic methods of treating petroleum fluids such as straight run and cracked gasolines, pressure distillates, naphthas, polymerized gasolines and natural gasolines, such petroleum fluids being referred to hereafter as gasoline stock.

This application is a division of my co-pending application, Serial No. 104,304, filed October 6, 1936, now U. S. Patent 2,206,921.

In a more specific sense an object of this invention is a process for treating such potential motor fuel components in the vapor form over a catalytic material to remove the organic sulfur compounds which are so deleterious to the octane number and lead response of such fuels.

Another object of this invention is a process for treating gasoline stock in the vapor form over a catalytic material to reduce its sulfur content and simultaneously increase its octane number, improve its antiknock characteristics and otherwise produce desirable refining effects.

A further object of this invention is the marked improvement in quality of the gasoline stock with only a small decrease in volume of product boiling within the same range as the untreated oil. This is in contradistinction to the large losses which occur in such conventional operations as thermal reforming of such oils.

A still further object of the invention is the production under certain conditions of a gasoline stock with both a higher specific gravity and a higher octane rating than the untreated stock, whereas cracking of oils in the established manner produces higher octane products but of lower specific gravity.

Another object of the invention is the production under certain conditions of a by-product gas relatively rich in hydrogen, such gas being quite useful in hydrogenation process as well as for many other purposes.

It is well known that motor fuel specifications call for much higher octane ratings now than formerly, and gasoline stocks are being subjected to extensive refining and reforming operations in order to meet these more rigid specifications. Since the advent of "Q" gasoline several years ago, large quantities of tetraethyl lead, also, have been added to gasolines to raise them to 70 octane number, the rating of the average house-brand gasoline at the present time. All of these practices are quite expensive.

More recently certain results showing the deleterious effects of impurities of the sulfur type on the octane number and lead response of motor fuels were published in an article by Schulze and Buell (Oil and Gas Journal, vol. 34, No. 21, p. 22 (1935)). Organic sulfur compounds of different types exist in varying percentages in all gasoline stocks and are present in unusually large amounts in those from West Texas and certain other regions. The form of combination of the sulfur also varies, e. g., mercaptans, alkyl sulfides, thiophenes and thiophanes. Some of these compounds are much more deleterious than others to the octane number and lead response of the motor fuels; hence the magnitude of the reduction in sulfur content may or may not be a criterion of the improvement in antiknock characteristics.

Schulze and Buell in an application, Serial No. 756,142, filed December 5, 1934, describe certain catalytic processes for removing these impurities from sulfur bearing petroleum oils, thereby obtaining marked improvement in octane number and lead response of such products as natural gasoline and refinery straight run, cracked and vapor recovery gasolines.

I have now discovered a rather superior catalytic material for effecting the decomposition of the deleterious organic sulfur compounds in hydrocarbon oils and gases. Solid adsorbent catalytic material consisting of zirconium oxide either alone or in admixture with alumina causes rapid decomposition of mercaptans, organic sulfides and the like to hydrogen sulfide when hydrocarbon vapors containing such impurities are passed over these contact masses. The zirconium oxide may be synthetically prepared or the naturally occurring minerals may be used, the latter not being quite as effective as the former. The zirconium oxide gel may, if desired, be mixed with other metallic oxides or impregnated with solutions of salts which may be subsequently reduced to the oxide form.

A typical process for simple desulfurization of gasoline stock consists in contacting the gasoline stock in vapor form at a temperature in the range of about 500° to 800° F. which eliminates a part or all of the sulfur from mercaptans, alkyl sulfides, etc., as hydrogen sulfide. The hydrocarbons are then freed of hydrogen sulfide by a caustic wash or other suitable means. Completely sweetened products can be obtained in this manner. The following example is given as merely illustrative of the results obtained by this invention and shall in no sense be interpreted as a limitation of the invention.

Composite cracked gasoline from Panhandle topped crude was contacted with zirconium oxide catalyst at a temperature of 735° F. and a flow

rate above three liquid volumes per hour per volume of catalyst. For comparative purposes, another portion of the gasoline was treated under similar conditions with bauxite. A considerable improvement in lead response resulted with the bauxite treatment but the zirconia gave even a greater one. The decomposed impurities were removed in each instance prior to determination of octane ratings.

	Undesulfurized	Bauxite desulfurized	Zirconia desulfurized
A. S. T. M. octane number (0 cc. TEL)	58.2	58.8	59.9
A. S. T. M. octane number with 0.5 cc. TEL	62.2	63.2	64.8
A. S. T. M. octane number with 1.0 cc. TEL	65.4	67.0	68.4
A.S.T.M. octane number with 2.0 cc. TEL	69.5	71.5	72.4
Sulfur content	0.096	0.063	0.061

I have discovered also that still greater improvement in antiknock characteristics can be obtained when the gasoline stocks are treated under the conditions specified below. In addition to the removal of the organic sulfur impurities which are so deleterious to the octane number and lead response of the gasoline stock, or the motor fuel made therefrom, certain reactions which involve still other deleterious impurities and/or low octane number compounds are made to take place while in contact with catalysts comprising zirconia; therefore, the treated product has an octane number considerably higher than that produced merely by the removal of the organic sulfur.

In one specific embodiment of this process which yields the combined advantages noted above, the gasoline stock is passed in the vapor form over a well dehydrated zirconium catalyst at a temperature in the range of about 900° F. to 1200° F. and at a flow rate of 1 to 100 liquid volumes per hour per volume of catalyst. For example, at a temperature of 1000° F. to 1025° F. the preferred flow rate is of the order of 1 to 10 liquid volumes per hour per volume of catalyst. At higher temperatures shorter contact times are sufficient; therefore, flow rates as high as 100 liquid volumes per hour per volume of catalyst may be employed.

I have discovered that in treating gasoline stocks in the vapor form over zirconia catalyst there are specific temperature ranges for the reactions involving the decomposition of those compounds responsible for the low octane rating of the gasoline. As stated above, at temperatures of 500° to 800° F. the organic sulfur compounds such as mercaptans, alkyl sulfides, etc., are decomposed into hydrogen sulfide without any substantial decomposition of the hydrocarbon constituents, at temperatures in the range of 800° to 900° F. there is little or no additional improvement in octane number over that obtained in the simple desulfurization treatment, but at temperatures above 900° F. a second series of reactions takes place as evidenced by the formation of large quantities of hydrogen gas and by the marked increase in octane number of the treated gasoline stock.

This marked improvement in octane number which results from the treatment at temperatures above 900° F. is not due to "cracking" in the usual sense of the word, since in the absence of the zirconia catalyst and under otherwise similar conditions of temperature and contact time there is no appreciable change in the characteristics of the gasoline stock. Furthermore, the improvement which results from the treatment with zirconia catalysts under the conditions mentioned is not due to an accelerated reforming similar to that occasioned by the presence of adsorbent porous material sometimes referred to as material of the clay type. For example, when the same gasoline stock is contacted at these temperatures above 900° F. with fuller's earth under identical conditions of temperature, pressure and contact time the improvement is almost nil as compared with that obtained with the zirconia catalysts.

In the operation of this process high pressures are not needed, extremely good results being obtained in the range of atmospheric to 100 pounds. Higher or lower pressures may, of course, be employed wherever economic conditions warrant them. In practice it is usually desirable to use pressures somewhat above atmospheric so that the vapors can be conducted directly to a fractionator or to treating tanks for final processing.

Following the treatment of the vapors over the catalyst the decomposed impurities and light gas fraction are separated from the gasoline hydrocarbons by fractional condensation or any other conventional means. If desired, the uncondensed light gas fraction may be passed through a vapor recovery plant of the absorption or other conventional type whereby the hydrocarbons other than methane may be recovered and made useful for other purposes. Also the decomposed impurities may be removed by chemical means in a step apart from that of removal of the hydrogen and low boiling hydrocarbons from the gasoline hydrocarbons.

A typical example of the operation of this process above 900° F. is given as illustrative of the results which have been obtained in the treatment of various gasoline stocks, but this example is in no sense to be interpreted as limiting the invention.

Refinery high end-point straight run gasoline from Panhandle crude oil was contacted in the vapor form with dehydrated zirconia catalyst maintained at a temperature of 1000° F. and a flow rate of about 2 volumes of liquid gasoline per hour per volume of catalyst. After removal of the decomposed impurities and the light gas fraction by fractionation or any other conventional means the following remarkable improvement was noted.

	Before treatment	After treatment
A. S. T. M. octane number (0 cc. TEL)	46.8	57.3
A. S. T. M. octane number with 1.0 cc. TEL	55.7	67.9
A. S. T. M. octane number with 2.0 cc. TEL	60.9	73.7
A. S. T. M. octane number with 3.0 cc. TEL	65.1	76.8
Sulfur content, percent	0.075	0.027
Specific gravity	.7351	.7366
Reid vapor pressure	7.80	9.75
Unsaturation, mol percent	0.2	6.4
Engler distillation:		
10% evaporated, °F.	156	151
50% evaporated, °F.	255	246
95% evaporated, °F.	394	395

The fixed gas formed during the treatment of this gasoline amounted to 235 cu. ft. (S. T. P.) per barrel of gasoline charged. The analysis of the gas was as follows: hydrogen, 71.4 per cent; carbon monoxide, 2.1 per cent; methane, 14.6 per cent; ethylene, 1.9 per cent; ethane, 3.9 per cent;

propylene, 2.7 per cent; propane, 3.4 per cent, and upon substantial removal of these hydrocarbons heavier than methane by essentially any suitable process or system, such as by the conventional absorption system, the residual gas contained 81 per cent hydrogen. The hydrogen amounted to 168 cubic feet per barrel of gasoline and the methane to 34 cubic feet, a hydrogen to methane ratio of 4.9. The gas loss calculated as weight per cent of the gasoline charged was only 2.18 per cent. The total loss in volume of gasoline boiling within the same range as the untreated was about 3 per cent. By this treatment the gasoline was made into a 70 octane number motor fuel merely by adding 1.33 cc. of tetraethyl lead (TEL) per gallon whereas the untreated gasoline made only a 65 octane number motor fuel with the addition of 3 cc. tetraethyl lead (TEL) per gallon.

I have found that in the treatment of gasoline stocks in the vapor form over zirconia catalysts in the temperature range of 900° to 1200° F., as shown in the example given above, considerable dehydrogenation of the hydrocarbons occurs. There is only a very slight amount of cracking, as evidenced by the small proportion of methane in the gas, providing, of course, the temperature and contact time are properly chosen, since it is obvious that substantially long contact times at temperature of 1100° F. and above will produce cracking. With proper choice of the temperature and contact time, however, it is possible by means of this invention to substantially avoid the formation of methane and other products of cracking. Hydrogen to methane ratios as high as 30 to 1, and sometimes higher, can readily be obtained.

I have found that although dehydrogenation of certain of the hydrocarbons occurs during the treatment of gasoline stocks with zirconia catalysts at temperatures above 900° F., this dehydrogenation is only one of several reactions taking place. It is evident from the results such as those given above that an improvement of 10.5 octane numbers could not have resulted merely by the conversion of 6.5 per cent of saturated aliphatic hydrocarbons to simple unsaturated hydrocarbons of the olefin type. Neither can it be accounted for on the basis of the amount of hydrogen formed. While I am not certain of the exact changes which occur during this treatment of gasoline stocks over a catalyst of the peculiar nature of zirconium oxide, I believe the remarkable improvement in octane number results from several concurrent reactions, namely, (1) decomposition of deleterious organic sulfur compounds to hydrogen sulfide which may be removed, (2) decomposition and subsequent removal of impurities other than the sulfur type, (3) dehydrogenation of hydrocarbon constituents, and (4) changes in molecular structure of certain of the hydrocarbons. The extent of the improvement from each of these sources varies, of course, with the gasoline stock being treated.

In the practice of the present invention the zirconium oxide or the zirconia like material is crushed to a suitable size, usually 10 to 30 mesh. If desired it may be diluted with active or inactive substances. Particularly active catalytic masses may be prepared from intimate mixtures of zirconia and alumina gels. Either one of these gels impregnated with a salt solution of the other gives on drying and on conversion of the salt to the oxide form a very satisfactory catalyst. Bauxite impregnated with a solution of a zirconium salt, usually converted to the oxide in a subsequent step, has high activity.

Synthetic zirconium hydroxide gel usually contains a large proportion of water which is driven off by heating at elevated temperatures. In the practice of my process for the treatment of gasoline stocks to obtain desulfurization, dehydrogenation and the like concurrently, best results are obtained with rather thoroughly dehydrated zirconia catalysts. The first step in this process usually consists, therefore, in dehydrating the zirconia, preferably in situ, by raising the temperature gradually to the temperature of operation or higher while a slow stream of air or hydrocarbon gas is passed over it. Vacuum drying may be done, if desired. This step of passing air or hydrocarbon gas over the catalyst can obviously be omitted in practice, and the gasoline vapors started immediately over the zirconia. Much of the improvement in the gasoline stock will be lost, of course, during the first few hours of operation in this manner, or until the working temperature has been reached and the catalyst has been dehydrated.

It has been found that the zirconia catalysts gradually lose their catalytic activity with use but they may be reactivated indefinitely by burning out the carbonaceous residues in situ with steam and air, or an oxidizing gas, or by burning in a furnace.

It has been found that the hydrogen-bearing gas which is formed during the treatment of gasoline stocks according to my invention may be recycled through the system by adding such gas, or a portion of it, to the gasoline vapors prior to passage over the catalyst. Such hydrogen gas should, of course, not be allowed to pyramid too much or the reactions may be unfavorably influenced. Also in processing gasoline stocks containing appreciable quantities of sulfur compounds, the hydrogen sulfide should be removed from the gas prior to recycling.

Obviously the hydrogen gas produced as a by-product in my process has considerable economic value. A gas containing more than 80 per cent, and up to 95 per cent hydrogen and the balance methane can be readily obtained by applying simple extraction methods for the removal of the small amount of hydrocarbons higher than methane. Concentrations of hydrogen higher than 95 per cent can be obtained by more elaborate extraction methods. In any event hydrogen for hydrogenation and/or other purposes can be obtained in this treatment of gasoline stocks over zirconia catalysts at extremely low cost. A very distinct advantage of my process is the formation of relatively large quantities of hydrogen from such hydrocarbons as those of the aliphatic series with methane being the only impurity in appreciable amount. Obviously this gas can be utilized for many purposes where the more common mixture of hydrogen and carbon monoxide cannot be tolerated at any cost.

If desired, the gasoline stock vapors may be given two or more successive treatments with the zirconia catalytic materials in a series of catalyst towers, or the vapors or any fraction thereof may be recycled with the fresh vapors through the catalyst tower. Some additional heat, also, may be supplied to the vapors prior to the second and/or successive catalytic treatments.

The gasoline stocks after treatment at desulfurizing temperatures of 500 to 800° F. may or may not need a subsequent treatment to remove colored and gum forming constituents. At tem-

peratures of 900° to 1200° F. whereby desulfurization, dehydrogenation and the like are obtained concurrently, the stocks usually require a subsequent treatment to remove small amounts of colored and gum forming constituents in order to make them suitable as motor fuel. This final purification step may be carried out in conventional manner.

The foregoing specification and examples have disclosed and illustrated the invention, but since it is of generally wide application and the number of examples of results obtainable by its use might be multiplied greatly neither is to be construed as imposing limitations upon the scope of the invention. The term gasoline stocks as used herein includes natural gasolines, refinery straight run, cracked and vapor recovery gasolines, polymerized gasolines, naphthas, pressure distillates, and/or mixtures or blends of any two or more of these or of similar hydrocarbon mixtures. Light gases associated with such stocks may be treated along with the hydrocarbons boiling within the gasoline range, or, if desired, such gases may be treated alone.

I claim:

1. A process of improving the antiknock characteristics of a gasoline stock, comprising contacting said gasoline stock in vapor form with a dehydrated solid adsorbent catalytic material consisting of zirconium oxide and bauxite at a temperature in the range of 900° to 1200° F. under pressures between atmospheric and 100 pounds per square inch and at a flow rate of about 1 to 100 liquid volumes of gasoline stock per hour per volume of catalyst, separating the decomposed impurities and the light gas fraction high in hydrogen gas from the hydrocarbons boiling in the gasoline range, and thereby obtaining a gasoline stock with an equivalent boiling range having improved antiknock characteristics.

2. A process of improving the antiknock characteristics of a gasoline stock, comprising contacting said gasoline stock in vapor form with a dehydrated solid adsorbent catalytic material consisting of zirconium oxide and alumina at a temperature in the range of 900° to 1200° F. under pressures between atmospheric and 100 pounds per square inch and at a flow rate of about 1 to 100 liquid volumes of gasoline stock per hour per volume of catalyst, separating the decomposed impurities and the light gas fraction high in hydrogen gas from the hydrocarbons boiling in the gasoline range, and thereby obtaining a gasoline stock with an equivalent boiling range having improved antiknock characteristics.

3. A process of treating petroleum hydrocarbons boiling within the range of gasoline which comprises catalytically increasing the anti-knock value of said hydrocarbons, without substantial alteration of the boiling range thereof, by passing said hydrocarbons in vapor phase at a temperature of the order of 900° F. over a catalyst consisting essentially of zirconium oxide.

4. A process of treating petroleum hydrocarbons boiling within the range of gasoline which comprises catalytically increasing the antiknock value of said hydrocarbons, without substantial alteration of the boiling range thereof, by passing said hydrocarbons in vapor phase at a temperature between approximately 900° F. and 1025° F. over a catalyst consisting essentially of zirconium oxide.

5. A process of treating petroleum hydrocarbons boiling within the range of gasoline which comprises catalytically increasing the antiknock value of said hydrocarbons, without substantial alteration of the boiling range thereof, by passing said hydrocarbons in vapor phase and at a temperature between approximately 900° and 1200° F. over a catalyst consisting essentially of zirconium oxide.

6. A process of treating petroleum hydrocarbons boiling within the range of gasoline which comprises catalytically increasing the antiknock value of said hydrocarbons, without substantial alteration of the boiling range thereof, by passing said hydrocarbons in vapor phase and at a temperature in the range of 900°–1200° F. over a catalyst consisting essentially of zirconium oxide, removing colored and gum forming constituents from the hydrocarbons so treated, and recovering a gasoline stock having improved antiknock characteristics.

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