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METHOD OF IMPROVING KNOCK RATING OF NAPHTHAS

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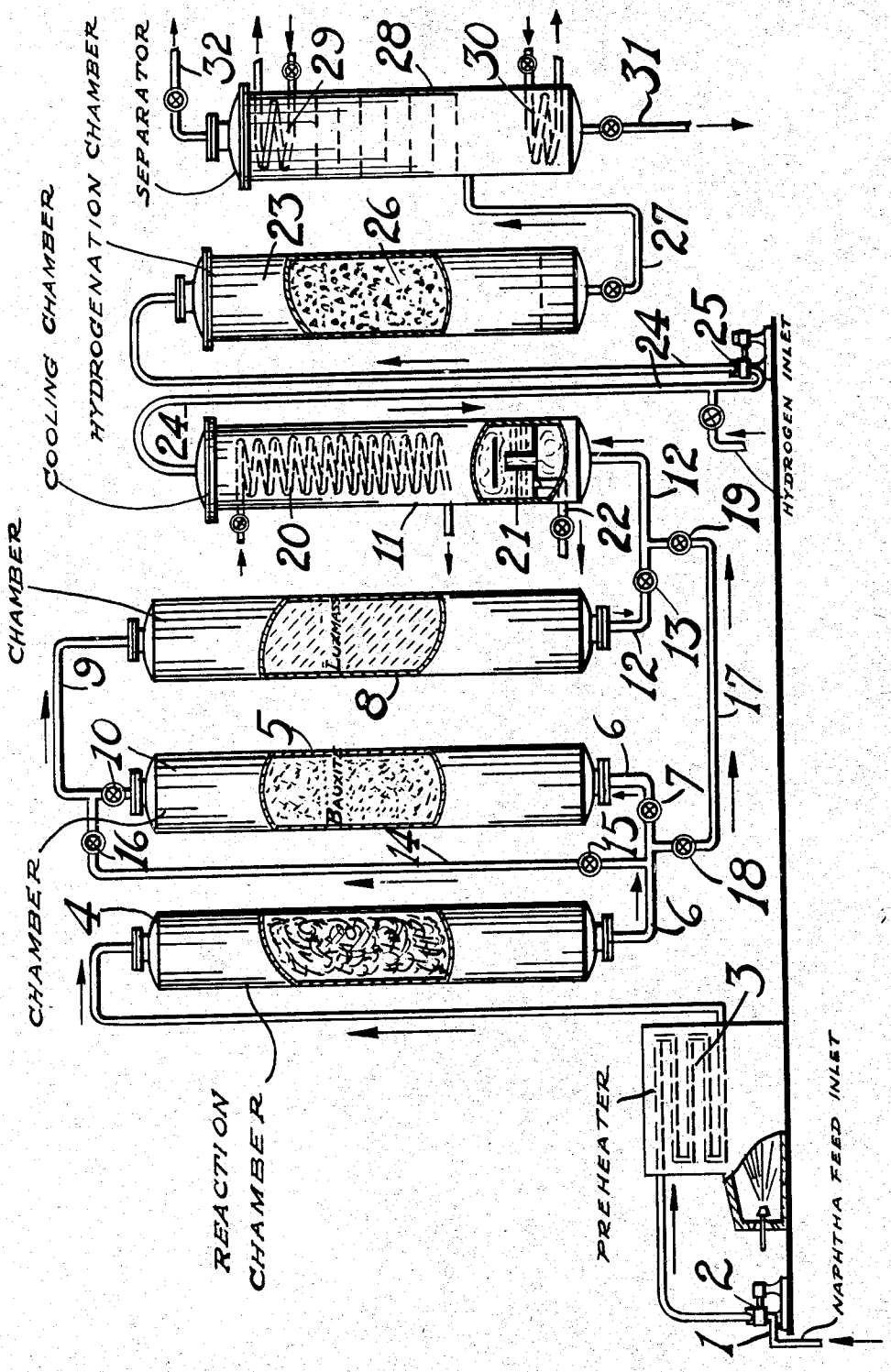

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METHOD OF IMPROVING KNOCK RATING OF NAPHTHAS

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The present invention relates to a method for improving the octane number of naphthas. It includes a process for so improving naphthas containing naphthenics and open chain hydrocarbons by subjecting said naphtha successively to a catalytic dehydrogenation and to a controlled hydrogenation. This embodiment of the present invention is applicable to naphthas from any source, particularly to naphthas formed by the polymerization of normally gaseous hydrocarbons, insofar as these naphthas contain both naphthenic and open chain hydrocarbons.

The present invention also includes the application of the controlled hydrogenation to a naphtha from any source having a composition analogous to that obtained by the dehydrogenation of the afore-described naphthas, that is, containing aromatics and open chain olefines.

A number of methods for reforming naphtha so as to increase its octane number are known in the art. Most of these methods consist of high temperature treatments with or without a catalyst to increase the octane number of the naphtha either by splitting off hydrogen from naphthenic constituents thereof or by increasing the content of light ends in the naphtha.

It has now been found that a larger increase in octane number than was attainable by the methods hitherto practiced can be achieved by a multi-stage treatment of a naphtha of the type referred to above, in the first stage of which the naphthenic constituents are converted into aromatics and in the second stage of which the naphtha is treated with hydrogen under conditions suitable for the hydrogenation of olefins to paraffins. Special advantages of this combination are that the heat contained in the naphtha leaving the first stage is more than sufficient to maintain the dehydrogenated naphtha entering in the second stage at the desired preheated condition, and that the hydrogen evolved in the first stage is usually sufficient for the treatment in the second stage.

Reforming catalysts may be divided into two general groups, those which accelerate dehydrogenation typified by oxides, sulfides, and other compounds of metals of Group VI of the periodic system, which may be employed alone but are preferably associated with other difficultly reducible oxides, such as alumina, thoria, ceria, etc., and those which have a so-called debutanizing effect because they accelerate the splitting off of butane in preference to hydrogen, typified by activated alumina and marsil clay. In the first stage of the process of the present invention, catalysts of the first type are employed, particularly a mixture of zinc, lead and chromic oxides on magnesia, chromic oxide on alumina, or a sulfide of a metal of Group VI, such as molybdenum or tungsten sulfide.

The conditions to be employed in the first stage of the present process are well known, and may be stated, in general terms, to be the employment of a temperature ranging from 850° F. to 1100° F. atmospheric or slightly superatmospheric pressure, and space velocities ranging from 0.2 to 2.0 cu. ft. of liquid feed per cu. ft. of catalyst per hour. The proper space velocity for any given set of conditions is best determined by measuring the molecular weight of the fixed gases evolved in the treatment. This value should be kept as low as possible, since substantial carbon-carbon splitting is to be avoided. The preferred space velocity is that which gives the highest octane number improvement with the smallest increase in the molecular weight of the fixed gases produced.

The range of temperatures to be employed in the second stage of the process is considerably lower than that employed in the first stage, ranging from about 200° to about 580° F. In this stage elevated pressure is desirable. The only upper limit on the pressure to be employed is that dictated by economical operation. Generally, it may be said that pressures ranging from 50 to 200 lbs./sq. in. will be satisfactory, altho when sulfur-immune hydrogenation catalysts, such as those containing compounds of metals of Group VI, are employed, the pressure will preferably range upwardly of 100 atmospheres, and is, preferably, between 200 and 300 atmospheres. Since pressure is necessary in the second stage, it is usually desirable to employ, in the first stage, as high a pressure as possible without unduly increasing coke formation and minimizing octane number improvement. A satisfactory operation is one in which a pressure of 100 lbs./sq. in. is maintained in both stages.

Since the temperature employed in the second stage is usually much below that at which coking of the hydrocarbons can occur, it is possible to employ, in the second stage, catalysts which have greater activity for hydrogenation than the catalysts which must be employed in the first stage to minimize coke formation. Suitable catalysts for the second stage are finely divided

nickel or copper, alone or supported on carriers, such as pumice or difficultly reducible oxides, such as alumina, ceria, thoria, chromic oxide, etc. The life of these catalysts, which are poisoned by sulfur, may be increased by removing from the feed stock any sulfur which it may contain. This is suitably accomplished by passing the vaporous products from the first stage over bauxite or iron sulfide before introducing them to the second reaction zone.

The hydrogen sulfide formed in the desulfurization step may be removed by contacting the products from the desulfurization zone with luxmass (hydrated iron oxide), metallic iron, or metallic copper, prior to the introduction of these products into the hydrogenation zone without the necessity of reducing the temperature. If desired, a sufficient amount of sulfur dioxide can be added to the products of the desulfurization zone to react with the hydrogen sulfide so as to convert it to free sulfur and water, the sulfur being condensible under the pressure necessary for the hydrogenation without a reduction of temperature below that suitable for the hydrogenation step. In many cases the reforming catalyst, employed in the first stage, effects sufficient desulfurization so that a separate desulfurization step may be omitted. Of course in the event that the catalyst in the second stage is the same as the catalyst in the first stage, and is sulfur-immune, the desulfurization step is not necessary. Such catalysts, however, require the employment of a higher temperature within the range specified than do catalysts which are poisoned by sulfur.

As previously stated, the hydrogen evolved in the first stage is reintroduced into the naphtha in the second stage. In order to insure as complete an improvement in the octane number of the naphtha as possible, it is usually desirable to provide for the addition of further quantities of hydrogen prior to the second stage.

It is not clearly understood with what constituents of the naphtha the hydrogen combines. It is known, for example, that benzol may be hydrogenated under the conditions employed in the second stage of the present process. Nevertheless, the second stage of the present process imparts an improvement to the octane number of the naphtha, thereby strongly indicating that the aromatics are no rehydrogenated. On the other hand, it is known that branched chain olefins have a lower octane number than the corresponding paraffins, whereas the straight chain olefins have a better octane number than the corresponding paraffins. These facts support the conclusion that in the second stage of the process of the present invention the branched chain olefins are selectively hydrogenated and this may be accounted for on the theory that the branched chain olefins have a greater affinity for hydrogen than do aromatics or straight chain olefins.

It follows that care has to be exercised in the second stage of the process of the present invention to avoid the rehydrogenation of aromatics and, if possible, straight chain olefins. The reaction can be controlled with a fair degree of accuracy by basing the duration of the hydrogenation treatment on bromine number reduction. In actual operation hydrogenation conditions suitable for the hydrogenation of olefins are selected, and any suitable hydrogenation catalyst is employed. If the hydrogenation step is a continuous operation, a rate of flow of the reactants is selected and the bromine number of the product at this rate of flow is determined and compared with the bromine number of the naphtha fed to the hydrogenation. Any rate of flow at which a substantial reduction in the bromine number is effected, is suitable. It is, of course, preferred not to reduce the bromine number to zero, since this would mean that all of the straight chain olefins would also be hydrogenated. Moreover, if the product of the hydrogenation step showed a zero bromine number, it would be impossible to conclude that the rate of flow employed to produce that product was not sufficiently slow to effect a rehydrogenation of the aromatics. Consequently, it is advisable to select such a rate of flow as will effect a substantial reduction in bromine number without reducing it to zero.

It is, of course, not easy to determine by this method a rate of flow such that only the branched olefins are hydrogenated. This is not a serious objection, however, because even though the hydrogenation of some of the straight chain olefins might reduce the octane number of the product from the hydrogenation step to a value below that of the feed of the hydrogenation step, it always results in an increase in the lead susceptibility of the naphtha so that upon the addition of lead, which is customary practice, the hydrogenated fuel will have a greater octane number than the feed to the hydrogenation step. After the hydrogenation unit has been in operation for some time, the rate of flow of the reaction material thru the unit can be adjusted with a fair degree of accuracy so as to effect the hydrogenation of only the branched chain olefins by plotting bromine number determinations against octane number determinations. In general, it may be stated that the bromine number reduction which gives the greatest increase in clear octane number is that reduction which is obtained when the branched olefins are hydrogenated to the exclusion of straight chain olefins.

When the hydrogenation is conducted as a batch operation, which is rarely the case in commercial practice, the duration of treatment can be likewise determined by test runs followed by bromine number determinations. Here, as in the case of the continuous operation, the duration of treatment selected is one which substantially reduces the bromine number without reducing it to zero, and is preferably that duration of treatment which gives that reduction in bromine number which is accompanied by the greatest increase in octane number.

As is apparent from the above discussion, the present invention is based, to a large extent, upon the discovery of the fact that in a mixture of straight chain and branched chain olefins and aromatics, branched olefins can be hydrogenated to the exclusion of the other unsaturated constituents, under conditions which are suitable for the hydrogenation of all the constituents but for a period shorter than that required for the hydrogenation of all of them. Consequently, there is contemplated, within the scope of the present invention, the improvement of the octane number of any gasoline containing branched olefins together with straight chain olefins or aromatics by a controlled hydrogenation carried out under conventional hydrogenation conditions for a period of time determined by bromine number reduction. There is also contemplated the improvement in the lead susceptibility of any gasoline containing straight chain olefins and aro-

matics by a similarly controlled hydrogenation. This embodiment of the present invention is particularly applicable to a gasoline which has been stored for a long period. Especially one which has been stored after being catalytically reformed.

The treatment with hydrogen not only exerts a marked influence upon octane number and/or lead susceptibility, but also has an extremely beneficial effect upon copper dish gum and the breakdown characteristics of the gasoline. Breakdown time is determined by placing a test tube containing 25 cc.'s of gasoline in a bomb of specified size, feeding oxygen into the bomb at atmospheric temperature until 100 lbs. oxygen pressure has been built up, and then heating the bomb in a steam bath. The pressure builds up to a maximum and then begins to drop. The time intervening between the point at which the maximum pressure is reached and the point at which the pressure has dropped 2 lbs. from the maximum pressure is designated as the breakdown time. The breakdown time of the gasoline is a direct measure of the stability of the gasoline in storage.

A front elevation of an apparatus suitable for carrying out the process of the present invention is illustrated in diagrammatic form in the accompanying drawing in which 1 is a feed line thru which naphtha may be passed after being put under pressure by pump 2, if desired, into preheater 3, then into reaction chamber 4 containing a suitable catalyst of the hydrogen splitting type, and maintained at a temperature suitable for catalytic reforming. Chamber 4 is connected to chamber 5, which contains bauxite or any other desired desulfurization catalyst, by a line 6 provided with a valve 7. Chamber 5 is connected to a chamber 8, containing luxmass, metallic iron, or metallic copper, by line 9 provided with a valve 10. Chamber 8 is connected to a cooling chamber 11 by a line 12 provided with a valve 13. Line 6 is connected to line 9 by a pipe 14 provided with valves 15 and 16. Line 6 is also connected to line 12 by a branch line 17 provided with valves 18 and 19.

Chamber 11 is provided with a coil 20 which may be employed either as a cooling or a heating means, the latter, in case the reaction mixture, in passing thru chambers 5 and 8, is cooled to a temperature below that preferred for the hydrogenation step. A liquid collecting tray 21 is provided in chamber 11 and a draw-off line 22 for liquids is suitably arranged in draining relation to said tray.

Chamber 11 is connected to hydrogenation chamber 23 by line 24 in which is arranged a pump 25 by which the desired pressure may be imposed upon the reaction material in case preceding steps are conducted under a lower pressure. Chamber 23 is filled with a catalyst 26 of the type heretofore described. The products from chamber 23 pass thru line 27 into separator 28 provided with a cooling coil 29, a heating coil 30, a draw-off 32 for normally gaseous products and a draw-off 31 for finished naphtha.

In the event that it is desired to further desulfurize the reformed naphtha, valves 7, 10 and 13 are opened and valves 15, 16, 18 and 19 are closed. If it be only desired to remove hydrogen sulfide from the product leaving the reforming chamber, valves 15, 16 and 13 are opened and valves 7, 10, 18 and 19 are closed. When no sulfur removal is necessary, valves 18 and 19 are opened and valves 7, 13 and 15 are closed.

Example I.—In a specific application of the process of the present invention, a West Texas straight run naphtha having a 400 end point was fed at atmospheric pressure at a rate of 0.534 cc.'s per hour per cc. of catalyst at a temperature between 1000 and 1060° F. over a catalyst composed of chromium, lead and zinc oxides. The gasoline yield varied between 89.3 and 95% by volume of the feed, the gas loss was between 5.1 and 8.2% by weight of the feed and the hydrogen produced was between .45 and 1.1% by weight of the feed. The product had an octane number which varied between 67 and 69, a bromine number of 0.28 and a gum content as measured by the copper dish test of 500 mg. per 100 cc.'s and a breakdown period of 0.4 hour. The vaporous product containing free hydrogen was fed to a bomb where it was mixed with an additional 12 liters of hydrogen per liter of vaporous product and placed under a pressure of 800 lbs./sq. in. The bomb contained a catalyst composed of copper, manganese oxide and zinc oxide, and was heated to 175° C. at which it was maintained for two hours. The product so obtained had a bromine number of 0.18, a gum content measured by the copper dish method of 82 mg./100 cc.'s, a breakdown period of 5.6 hours and a clear octane number of 72.

Example II.—A sample of the reformed West Texas naphtha resulting from the first stage of the process described in the preceding example was stored for about a year, at the end of which time it had a bromine number of 0.28, a gum content measured by the copper dish method of 1261.6 mg./100 cc.'s, a breakdown period of 0.4 hour and a clear octane number of 56. This naphtha was agitated with bone black and filtered and then hydrogenated under the conditions and for the same length of time as the reformed product in Example I. The product of this treatment had a bromine number of 0.18, a gum content measured by the copper dish method of 61.6 mg./100 cc.'s, a breakdown period of 4.8 hours and a clear CFR MM octane number of 59.4.

Example III.—A West Texas straight run naphtha of different origin from that employed in Example I and having a clear octane number of 42 was catalytically reformed under the conditions described in Example I. The resulting product had a bromine number of 0.31, a gum content measured by the copper dish method of 266 mg./100 cc.'s, a breakdown period of 0.4 hour, a clear CFR MM octane number of 65.7 and an octane number with 3 cc.'s of lead tetraethyl/gal. of 78.8. When this product was hydrogenated, as described in Example I, under the same conditions and for the same length of time, it had a bromine number of 0.14, a gum content measured by the copper dish method of 245 mg./100 cc.'s, a breakdown period of 2.4 hours, a clear CFR MM octane number of 63.2 and an octane number with 3 cc.'s of lead tetraethyl/gal. of 80. It is to be noted that the clear octane number of the hydrogenated product in this run was less than that of the reformed product, while the lead susceptibility of the latter was distinctly superior to the former. This indicates that the period employed for hydrogenation was somewhat too long and resulted in the hydrogenation of some of the straight chain olefins. This is borne out by the fact that in this run the bromine number of the reformed product was reduced by .17 whereas the bromine number of the hydroformed product in the first example was reduced by hydrogenation only .10.

The method of determining the bromine numbers given in the above examples was according to the Buc-Seaman modification of the Francis method. From 5 to 10 grams of solid KBr is introduced into a glass stoppered flask, the required volume of

$$\frac{N}{2}KBrO_3\text{–}KBr$$

added as determined by a trial titration. To this was added 20 cc. of 10% H_2SO_4 saturated with KBr. Allow three minutes for liberation of bromine, then add a measured amount, for example, 0.5 or 0.7 gram of the sample diluted with chloroform, and shake vigorously for exactly two minutes. Finally add 15 cc. of saturated KI solution and titrate the liberated iodine with

$$\frac{N}{10}Na_2S_2O_3$$

The bromine numbers given in the above examples were computed on the basis of grams of bromine per gram of naphtha.

The nature and objects of the present invention having been thus described and illustrated by examples, which are offered for the purpose of demonstrating the nature of the improvement effected by the present invention and not for the purpose of defining the limits of applicability of the present invention, what is claimed as new and useful and as desired to be secured by Letters Patent is:

1. In the process of producing a highly refined motor fuel by reforming a naphtha at temperatures between about 850° F. and about 1100° F. under superatmospheric pressures in the presence of a dehydrogenation catalyst wherein the resultant products contain branched chain and normal mono-olefins followed by a catalytic hydrogenation with hydrogen of the reformed naphtha, the improvement which comprises controlling the hydrogenation process within the temperature range of about 200 to about 580° F. under a superatmospheric pressure of at least 3 atmospheres and for a time sufficient to reduce the bromine number to no less than about 0.14.

2. Process as in claim 1 wherein said naphtha, having a bromine number of 0.28, is hydrogenated only until the bromine number is reduced to 0.18.

3. Process as in claim 1 wherein the naphtha is hydrogenated only until its original bromine number has been reduced between about 30 and about 60% and wherein the bromine number is at least 0.14.

4. A process which comprises dehydrogenating a straight run naphtha in the presence of a dehydrogenation catalyst at the rate of .534 cc. per hour per cc. of catalyst at a temperature between about 1000 and about 1060° F., mixing the resultant vaporous product with hydrogen and hydrogenating said product at about 800 lbs./sq. in. at a temperature of about 175° C. for about two hours in the presence of a hydrogenation catalyst.

5. A process for improving the motor fuel characteristics of naphtha containing substantial amounts of unsaturated hydrocarbons which comprises contacting said unsaturated naphtha in vapor phase with hydrogen in contact with a hydrogenation catalyst under hydrogenating conditions of time, temperature and pressure, and stopping the hydrogenation when the bromine number of the product is about 0.14.

6. A process for improving the motor fuel characteristics of naphtha containing substantial amounts of unsaturated hydrocarbons which comprises contacting said unsaturated naphtha in vapor phase with hydrogen in contact with a hydrogenation catalyst under hydrogenating conditions of time, temperature and pressure, and stopping the hydrogenation when the bromine number of the product is about 0.18.

7. A process for improving the motor fuel characteristics of naphtha containing substantial amounts of unsaturated hydrocarbons which comprises contacting said unsaturated naphtha in vapor phase with hydrogen in contact with a hydrogenation catalyst under hydrogenating conditions of time, temperature and pressure, and stopping the hydrogenation when the bromine number of the product is at least 0.14 but substantially below the bromine number of the unsaturated naphtha feed.

8. A process for improving the motor fuel characteristics of a reformed naphtha containing substantial amounts of aromatics, branched and straight chain mono-olefins, which comprises contacting said naphtha in vapor phase with hydrogen in contact with a hydrogenation catalyst under hydrogenating conditions of time, temperature and pressure, and stopping the hydrogenation when the bromine number of the product is about 0.14.

9. A process for improving the motor fuel characteristics of a reformed naphtha containing substantial amounts of aromatics, branched and straight chain mono-olefins, which comprises contacting said naphtha in vapor phase with hydrogen in contact with a hydrogenation catalyst under hydrogenating conditions of time, temperature and pressure, and stopping the hydrogenation when the bromine number of the product is about 0.18.

10. A process for improving the motor fuel characteristics of a reformed naphtha containing substantial amounts of aromatics, branched and straight chain mono-olefins, which comprises contacting said naphtha in vapor phase with hydrogen in contact with a hydrogenation catalyst under hydrogenating conditions of time, temperature and pressure, and stopping the hydrogenation when the bromine number of the product is at least 0.14 but substantially below the bromine number of the reformed naphtha feed.

11. A process which comprises hydrogenating a catalytically reformed West Texas straight run naphtha having a bromine number of about 0.31 in the vapor phase with hydrogen and hydrogenating said mixture at about 800 lbs./sq. in. at a temperature of about 175° C. for about 2 hours in the presence of a hydrogenation catalyst.

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