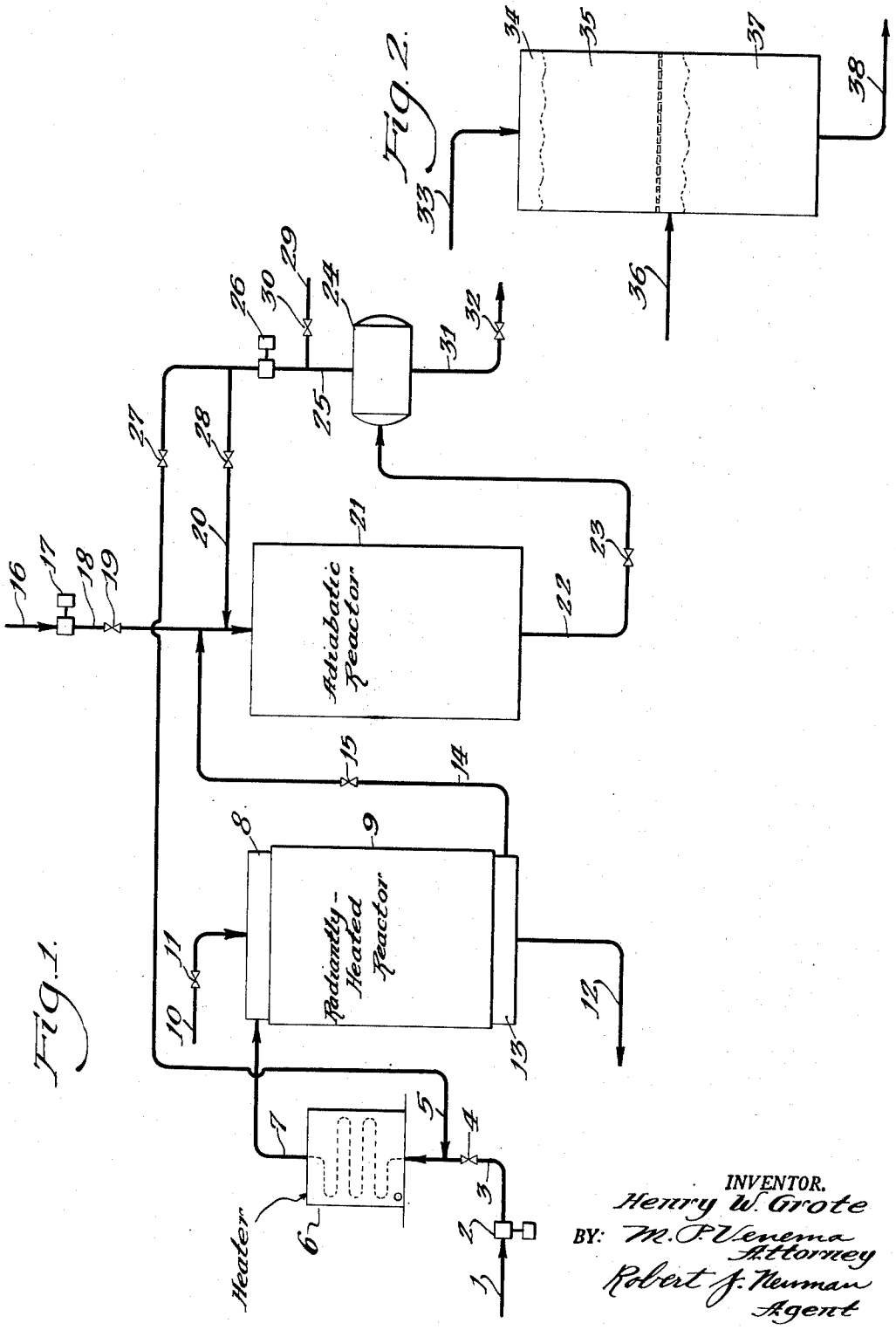
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METHOD OF CATALYTICALLY REFORMING HYDROCARBONS

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METHOD OF CATALYTICALLY REFORMING HYDROCARBONS

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1

This invention relates to the conversion of hydrocarbons. It is more specifically concerned with a particular method of simultaneously reforming hydrocarbon reactants of high and low naphthene contents in the presence of platinum-containing catalysts.

Hydrocarbon stocks of low octane number that boil approximately within the gasoline range and that contain naphthenes and paraffins may be upgraded by dehydrogenating the naphthenes to aromatics and hydrocracking the paraffins to lower boiling paraffins. The aromatics possess considerably higher antiknock ratings than the corresponding naphthenes; the same is true of the lower boiling paraffins relative to the higher boiling paraffins.

The yield-octane increase relationship resulting from aromatization is approximately linear over a wide range of octane increases. This is due to the loss of a portion of the charge stock to hydrogen, and in part to a density increase inherent in changing naphthenes to aromatics. Hydrocracking, on the other hand, involves a combination of cracking and hydrogenation of the fragments thereby produced. In the initial stages, this results in the formation of lower molecular weight gasoline hydrocarbons which are of lower density than the charge. Thus the initial octane increases due to hydrocracking often are obtained at a volumetric recovery or yield greater than 100%. As the reaction proceeds, however, there is an increase in the tendency to produce gaseous hydrocarbons, which results in a loss of yield without any appreciable increase in octane number. Hydrocracking, therefore, is an efficient reforming process when not carried to extremes. In general, to obtain the optimum yield at a given product octane number with a stock containing both naphthenes and paraffins, it is necessary to control the balance between the hydrocracking and aromatization reactions to limit the hydrocracking to the degree at which it is efficient and to obtain the remainder of the octane number increase by aromatization.

Since the same types of hydrocarbons that are susceptible to aromatization are also susceptible to hydrocracking, it is important that the aromatization reaction be carried out first, since if it is not, some of these particular hydrocarbons will be hydrocracked in the early stages, and it is impossible to obtain a maximum amount of aromatization or maximum yield for a given octane number. Therefore, with hydrocarbon reformer charging stocks that contain

2

both naphthenes and paraffins, I first subject the stock to dehydrogenation and thereafter to hydrocracking.

There are, however, some low octane number hydrocarbon stocks that boil within the gasoline range that are so low in naphthenes that it is not practicable to subject them to naphthene dehydrogenation. In accordance with my invention, I mix such a stock with the hydrogen rich effluent from the dehydrogenation zone and subject the resultant mixture to hydrocracking, i. e., I subject a stock containing naphthenes and paraffins to dehydrogenation and then commingle this stock with a low naphthene material and hydrocrack the resulting mixture. A combination process of this type offers a number of advantages. The dehydrogenation produces, for example, three molecules of hydrogen for each six membered ring naphthene. Inasmuch as only one molecule of hydrogen is required when one molecule of a paraffin is hydrocracked into two lower boiling paraffin molecules, it can be seen that the dehydrogenation of one molecule of naphthene produces sufficient hydrogen for the hydrocracking of three molecules of paraffin. Therefore, I am able to hydrocrack not only the paraffins in the effluent from the dehydrogenation zone but also the paraffins in the low naphthene hydrocarbon stock without resorting to the use of external hydrogen. I usually prefer to operate my combination process in such a manner that there is substantially no net consumption of hydrogen. This can be done by correlating the relative proportions of the two types of stocks fed to my process with the degree of dehydrogenation and hydrocracking obtained. Another advantage of adding a stock predominating in paraffins to the dehydrogenation zone effluent before it is subjected to hydrocracking, lies in the fact that the concentration of aromatics in the material passing through the hydrocracking zone is materially reduced. The presence of aromatics in the feed to the hydrocracker tends to cause carbon formation and the aromatics themselves tend to undergo certain reactions whereby a portion thereof is consumed without any benefit from an octane number standpoint. These tendencies are considerably reduced when the aromatic content is lowered to values below about 25% as they usually are in my process.

In one embodiment my invention relates to a hydrocarbon conversion process which comprises subjecting a naphthene-containing sub-

stantially olefin-free hydrocarbon reactant boiling below about 425° F. to the action of a dehydrogenation catalyst under dehydrogenation conditions, commingling the resultant product with a naphthene-lean, substantially olefin-free hydrocarbon reactant boiling below about 425° F., and subjecting the resulting mixture to the action of a hydrocracking catalyst maintained under hydrocracking conditions.

In a more specific embodiment my invention relates to a process which comprises contacting at aromatization conditions in a first reaction zone, a substantially olefin-free hydrocarbon reactant containing a substantial proportion of naphthenes and boiling approximately within the gasoline range with a catalyst predominating in aromatizing activity and comprising platinum and alumina, commingling the effluent from said first reaction zone with a hydrocarbon reactant of low naphthene content that predominates in paraffins, and contacting the resultant mixture at hydrocracking conditions with a catalyst possessing substantial hydrocracking activity and comprising platinum, alumina, and halogen.

The hydrocarbon stocks that may be converted in accordance with the present process by dehydrogenation followed by hydrocracking comprise nonolefinic hydrocarbons that contain naphthenes. By the term nonolefinic I mean substantially olefin-free, i. e., a few per cent of olefins can be present in the charge in some types of operation. Suitable stocks include narrow boiling fractions rich in naphthenes as well as substantially pure materials such as cyclohexane, and methylcyclohexane. Preferred stocks are those consisting essentially of naphthenes and paraffins, although relatively minor amounts of aromatics also may be present. This preferred class includes primarily straight-run gasolines, such as those from Trinidad and the Gulf Coast area. The gasoline may be a full boiling range gasoline having an initial boiling point within the range of from about 50° to about 100° F. and an end boiling point within the range of from about 325° to about 425° F. or it may be a selected fraction thereof which usually will be a higher boiling fraction, commonly referred to as naphtha, and generally having an initial boiling point of from about 125° to about 250° F. and an end boiling point within the range of about 350° F. to about 425° F. The expression "straight-run gasoline fraction" as used herein is intended to include both naphthas and full boiling gasolines.

The low naphthene content hydrocarbon stocks that are included only in the charge to the hydrocracking step should predominate in paraffins and will have about the same boiling ranges as the naphthene-containing stocks. Certain straight-run gasolines fall into this classification as well as some natural gasolines, recycle condensates, and the paraffinic gasolines produced by the Synthine process, i. e., by one or more of the modified forms of the Fischer-Tropsch process.

Any suitable naphthene dehydrogenation catalyst may be used in the first step of my process. Suitable catalytic composites include a compound of the metals of the left hand column of Groups V and VI of the periodic table and, in particular, the oxides of chromium, molybdenum, tungsten, and vanadium, either alone or in admixture with one another, and a suitable refractory supporting material such as alumina, magnesia, silica, or mixtures thereof. The particular process conditions of time, temperature, pressure and the like employed in any specific operation will, of course, vary somewhat depending upon the catalyst used in the operation.

Suitable hydrocracking catalysts that may be used in the second step of my process include composites comprising a cracking component plus a hydrogenating component. Examples of such composites are nickel, chromium, and molybdenum, deposited on or incorporated in silica-alumina, silica-zirconia, silica-magnesia, and the like.

The preferred type of catalyst for both the dehydrogenation and the hydrocracking steps is one comprising platinum and alumina. These catalysts may contain substantial amounts of platinum, but, for economic as well as for product yield and quality reasons, the platinum content usually will be within the range of from about 0.05% to about 5.0%. A particularly effective catalyst of this type contains relatively minor amounts, usually less than about 3% on a dry alumina basis, of a halogen, especially chlorine or fluorine. One method of preparing the catalyst comprises adding a suitable alkaline reagent such as ammonium hydroxide or carbonate to a salt of aluminum, such as aluminum chloride, aluminum sulfate, aluminum nitrate, and the like, in an amount sufficient to form aluminum hydroxides, which upon drying, can be converted to alumina. The halogen may be added to the resultant slurry in the form of an acid such as hydrogen fluoride or hydrogen chloride, or as a volatile salt such as ammonium fluoride or ammonium chloride. The amount of combined halogen in the finished catalyst determines the hydrocracking activity. Platinum-alumina catalysts that are substantially devoid of halogen predominate in dehydrogenation or aromatization activity; whereas platinum-alumina catalysts containing greater than about 0.3–0.5% halogen usually predominate in hydrocracking activity. The fluoride ion appears to be somewhat more active than other members of the halide group and, therefore, may be present in a lower concentration for a given degree of hydrocracking activity. Ordinarily the amount of halogen in the catalyst will not exceed about 3–5%.

A satisfactory method of adding platinum to the alumina-halogen composite comprises preparing a colloidal suspension of platinic sulfide by introducing hydrogen sulfide into an aqueous solution of chloroplatinic acid until said solution reaches a constant color, which usually is a dark brown. The resultant colloidal suspension of platinic sulfide is commingled with the aluminum hydroxide slurry at room temperature followed by stirring to obtain intimate mixing. The resulting material is then dried at a temperature of from about 200° to about 400° F. for a period of from about 4 to about 24 hours or more to form a cake. The resulting material may then be converted into pills or other shaped articles. Thereafter the catalyst may be subjected to a high temperature calcination or reduction treatment prior to use. It is to be understood that the foregoing method of preparing satisfactory platinum-alumina catalysts is merely illustrative and is not to be taken in a limitative sense inasmuch as various other methods may be employed to produce satisfactory catalysts of this type.

The use of the term "catalyst comprising platinum and alumina" in the specification and appended claims is intended to include platinum-

alumina composites of the type described above including those containing minor amounts of a halogen. The exact manner in which the halogen or halide ion is present in the catalyst is not known, although it is believed to be present in the form of a chemical combination or loose complex with the alumina and/or platinum components. Because the exact chemical constitution of such halogen-containing catalysts is not known, I sometimes refer to them as "catalysts comprising platinum, alumina, and a halogen." It is known, however, that the presence of a small amount of a halogen in the catalyst enhances the hydrocracking activity thereof; for platinum-alumina composites that are substantially halogen-free possess very little ability to provide hydrocracking.

Other platinum-containing catalysts that may be used in my process, although not necessarily with equivalent results, include platinum on charcoal, platinum on silica, platinum on asbestos, and platinum on bases or carriers that possess cracking activity such as silica-alumina composites. The corresponding palladium catalysts occasionally may be used with advantage in my process.

Additional features and advantages of my invention will be apparent from the following description of the attached drawing which illustrates a particular method for conducting a hydrocarbon reforming operation in accordance with the present invention.

Referring to Figure 1, a full boiling range straight-run gasoline which contains paraffins and a substantial amount of naphthenes is charged through line 1 and is picked up by pump 2, passed through line 3 containing valve 4, and is joined by a stream of recycle hydrogen flowing through line 5 and produced as hereinafter described. The combined stream of straight-run gasoline and hydrogen is passed through heater 6 wherein it is heated to a temperature of about 900° F. The effluent from the heater is withdrawn through line 7 and is changed to header 8 of reactor 9.

Reactor 9 comprises a furnace of the downdraft type and is provided with a burner at the top thereof. Vertically disposed tubes are arranged adjacent the wall of the furnace so as to be heated predominantly by radiant heat. A suitable gaseous or liquid fuel is charged to reactor 9 through line 10 containing valve 11 and the products of combustion are removed via line 12. The tubes are filled with ⅛" x ⅛" pellets of platinum-alumina catalyst containing less than about about 0.1% fluorine or chlorine. The tubes are disposed on an annular circle, the center of which substantially corresponds to the center of the combustion chamber. The flame and the products of combustion flow in a central longitudinal unobstructed path through the chamber substantially out of direct contact with said tubes. Because of the high heat input rates to the catalyst that can be obtained, a reactor of the type just described is particularly suitable for the highly endothermic naphthene dehydrogenation reaction. The amount of heat supplied to the catalyst and the reactants flowing therethrough ordinarily is approximately equal to the endothermic heat of reaction.

The effluent from the tubes in reactor 9 is passed through header 13 and into line 14 containing valve 15. The concentration of hydrogen in the effluent is considerably higher than the concentration of hydrogen in the charge to the

reactor because three molecules of hydrogen were liberated for each molecule of napthene that was dehydrogenated. The hydrogen-rich material flowing through line 14 is commingled with a heated stream of naphthene-lean gasoline which flows through line 16 and is picked up by pump 17 and passed through line 18 containing valve 19. A stream of recycle hydrogen flowing through line 20 is commingled with the two streams and the resulting mixture is passed into reactor 21. The reactor is packed with a platinum-alumina catalyst containing 0.5% fluorine and is maintained at a temperature of about 880° F. The predominant reaction that takes place in reactor 21 is hydrocracking of higher boiling paraffins to lower boiling paraffins. However, the catalyst possesses dehydrogenation activity, and the small amount of naphthenes that may be present in the effluent from reactor 9 or in the gasoline flowing through line 16 will be converted to aromatics in this zone. Consequently, the overall reaction that takes place in reactor 21 is substantially thermally neutral. However, it may be somewhat exothermic or even somewhat endothermic depending upon the relative amounts of hydrocracking and dehydrogenation that are effected.

The effluent from reactor 21 passes through line 22 containing valve 23 and into receiver 24 wherein a separation is effected between hydrogen and low molecular gaseous hydrocarbons on the one hand and higher molecular weight liquid hydrocarbons on the other. The hydrogen-rich gas is withdrawn from receiver 24 through line 25. It is picked up by compressor 26 and a portion is passed through line 5 containing valve 27 and the remainder is passed through line 20 containing valve 28. Make-up hydrogen may be added to or excess hydrogen may be withdrawn from the system through line 29 containing valve 30. The liquid hydrocarbon layer in receiver 24 is withdrawn through line 31 containing valve 32 and is sent to suitable fractionation and storage equipment.

It is to be understood that the process that has just been described is to be taken in an illustrative and not in a limitative sense for the reason that a number of variations may be made in the process without departing from the spirit of the invention. For example, in some types of operation it may be desirable to effect the dehydrogenation in reactor 9 in the absence of recycle hydrogen. Again, it may be desirable to combine the dehydrogenation zone and the hydrocracking zone into a single vessel as shown in Figure 2. The naphthene-rich reactant would then be passed through line 33 and into reactor 34 wherein it first contacts a bed 35 of dehydrogenation catalyst. The effluent from this bed is joined by a stream of naphthene-lean hydrocarbons passing through line 36 and the combined stream passes through bed 37 of hydrocarbon catalyst. The effluent from reactor 34 is withdrawn through line 38.

Hydrocarbon reforming operations carried out in accordance with my process in the presence of catalyst comprising platinum and alumina ordinarily will be conducted at temperatures of from about 750° F. to about 1000° F. The dehydrogenation reaction usually will be conducted at a temperature near the upper end of the range and the hydrocracking reaction will be conducted at a somewhat lower temperature within the range of from 750° F. to about 950° F. The pressure at which my process will be conducted

when employing platinum-alumina catalyst for the reforming of hydrocarbons usually will be within the range of from about 50 to about 1200 pounds per square inch; a weight hourly space velocity, which is defined as the weight of hydrocarbon charged per hour per weight of catalyst in the reaction zone, within the range of from about 0.2 to about 40; and the amount of hydrogen charged along with the hydrocarbons usually will be from about 0.5 to about 15 mols per mol of hydrocarbon. Higher partial pressure of hydrogen favors hydrocracking, consequently, the partial pressure of hydrogen in the hydrocracking zone ordinarily will be higher than in the dehydrogenation zone.

I claim as my invention:

1. A process for the simultaneous reforming of gasoline stocks of relatively high and low naphthene content, which comprises subjecting a substantially olefin-free straight-run gasoline fraction containing naphthenes and paraffins to catalytic dehydrogenation to convert naphthenes to aromatics and form hydrogen, commingling with the resultant hydrogen-containing product a substantially olefin-free, predominantly paraffinic, naphthene-lean gasoline fraction in an amount sufficient to lower the aromatic content of the mixture to below about 25%, and then subjecting the mixture to the action of a hydrocracking catalyst comprising platinum, alumina and halogen maintained under hydrocracking conditions to convert higher boiling paraffins into lower boiling paraffins.

2. The process of claim 1 further characterized in that said halogen comprises fluorine.

3. A process for the simultaneous reforming of gasoline stocks of relatively high and low naphthene content, which comprises subjecting a substantially olefin-free straight-run gasoline fraction containing naphthenes and paraffins to the action of a platinum-alumina catalyst at a temperature of from about 750° to about 1000° F. to convert naphthenes to aromatics and form hydrogen, commingling with the resultant hydrogen-containing product a substantially olefin-free, predominantly paraffinic, naphthene-lean gasoline fraction in an amount sufficient to lower the aromatic content of the mixture to below about 25%, and then subjecting the mixture to the action of a catalyst comprising platinum, alumina and halogen at a temperature of from about 750° to about 950° F. to convert higher boiling paraffins into lower boiling paraffins.

4. The process of claim 3 further characterized in that said halogen is fluorine.

HENRY W. GROTE.

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