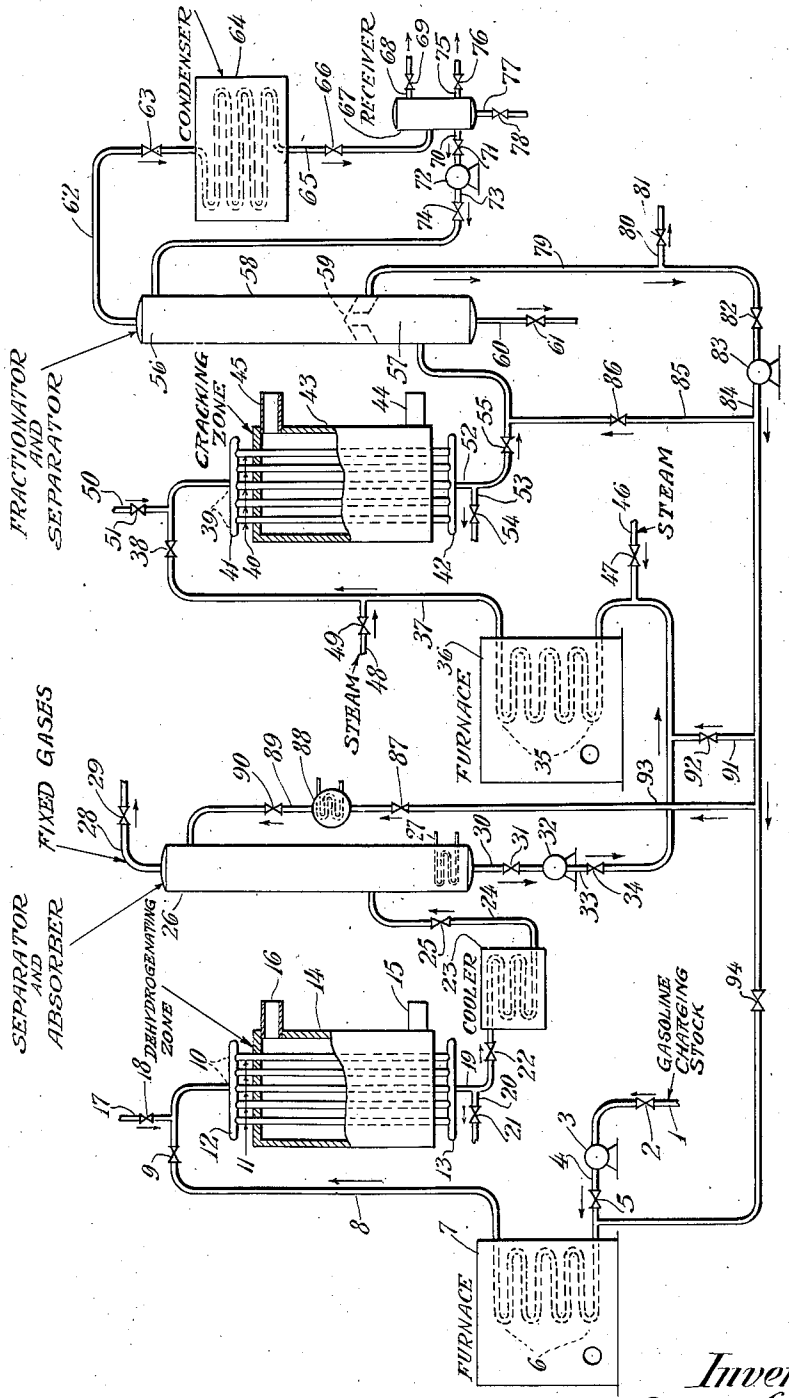
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CATALYTIC TREATMENT OF HYDROCARBONS

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CATALYTIC TREATMENT OF HYDROCARBONS

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This invention relates particularly to a process for converting straightrun hydrocarbon oils or paraffinic hydrocarbon oils boiling substantially in the range of gasoline which have a relatively low antiknock value into gasoline of relatively high antiknock value and/or normally gaseous hydrocarbons relatively rich in polymerizable olefins.

It has been previously found that straightrun gasolines or hydrocarbon oils predominately paraffinic in nature and boiling in the range of gasoline may be converted into oils containing substantial quantities of liquid olefinic hydrocarbons by subjecting them to contact with a dehydrogenating catalyst under selected conditions of temperature and pressure. Investigations have further shown that when the charging stock to a catalytic cracking process contains substantial quantities of olefinic hydrocarbons the yields of gasoline obtained approximate those obtained when running a stock predominately paraffinic and that the gases produced in the process contain higher percentages of olefins and particularly more isobutene. In addition, it has been found that lower cracking temperatures may be employed when the catalytic cracking stock contains substantial quantities of olefins, resulting in less deposition of carbonaceous materials on the catalysts and, therefore, longer catalyst life, because fewer reactivations are necessary to keep the catalysts in an active state. Furthermore, the lower temperatures employed in the catalytic cracking reaction conform more closely to the desired conditions for obtaining a greater degree of isomerization of the cracked products.

The present process is not limited to any particular type of charging stock, except with respect to those hydrocarbons boiling in the range of gasoline. It may, for example, be employed as a means for substantially completely gasifying the hydrocarbon oil charging stock. This particular feature is especially applicable when the charging stock consists of normal straight-chain paraffinic hydrocarbons containing 10 carbon atoms, or less, to the molecule, such as, for example, normal octanes or decanes which have a relatively low antiknock value. Hydrocarbons in this particular class of compounds, such as, for example, normal octane, when subjected to dehydrogenation yields a normal octane. A normal octane when subjected to contact with a cracking catalyst under selected conditions of temperature and pressure yields normal and iso-butene. The normal and iso-butene may then be subjected to polymerization to yield an iso-octane which after hydrogenation finds wide application as an aviation fuel.

Within the broad concepts of this invention dehydrogenation refers to the breaking of carbon-to-hydrogen bonds resulting in the splitting off of hydrogen from the molecule and the formation of a molecule containing a double bond, otherwise known as an olefinic hydrocarbon, whereas catalytic cracking refers to the breaking of carbon-to-carbon bonds resulting in the formation of two or more molecules of lighter hydrocarbons than the original.

In one specific embodiment the present invention comprises catalytically dehydrogenating hydrocarbon oils, separating the products into fixed gases and liquids, revaporizing said liquids and subjecting them to vapor phase catalytic cracking, introducing cooling oil consisting of reflux condensate to the cracked products, fractionating the mixture of cracked products and cooling oil to produce gases, vapors of gasoline boiling range which are condensed and collected, light reflux condensates used partly as said cooling oil and as recycle material to said vapor phase cracking and heavy residual materials which are removed from the process.

The outline of the process given in the preceding paragraph will be amplified in the following description to indicate its important features in greater detail by describing characteristic operations in connection with the attached diagrammatic drawing. The drawing illustrates one specific form of apparatus in which the process of the invention may be conducted. It is not drawn to any absolute or relative scale and the design and relative sizes of the individual units may be varied within reasonably wide ranges without departing from the broad scope of the invention.

Referring to the drawing, charging stock for the process, preferably comprising a straightrun gasoline or a paraffinic hydrocarbon oil boiling substantially in the range of gasoline, is directed through line 1 and valve 2 to pump 3 which discharges through line 4 containing valve 5 into heating coil 6. The hydrocarbon oil in passing through heating coil 6 is substantially completely vaporized therein and raised to the desired temperature without any substantial pyrolytic cracking thereof by means of heat supplied from furnace 7. The vaporized hydrocarbon oil discharged from heating coil 6 is directed through line 8 and valve 9 into catalytic reactor 10 and is contacted therein with a dehydrogenating cata-

lyst under substantially the same conditions of temperature and pressure as were employed on the outlet of the aforementioned heating coil.

Preferably and in the case here illustrated, catalytic reaction 10 comprises a plurality of small diameter reactor tubes 11 connected in parallel between upper and lower headers 12 and 13 and is disposed within a heating or cooling zone 14. In order to obtain the best results when dehydrogenating, which is an endothermic reaction (requiring heat), some form of heating must be employed in zone 14. It has been found that best results are usually obtained when employing fluid heating means, preferably comprising hot combustion gases, which may be introduced to zone 14 through duct 15, passed in indirect heat exchange relationship with the vapors in reactor tubes 11 and later discharged from the upper portion of zone 14 through duct 16.

In catalytic dehydrogenation, carbon deposits upon the catalysts as long as the vapors are in contact with it, and after a prolonged time the carbon deposition reaches such a point that the active surface of the catalyst exposed to the vapors is materially reduced. Frequent reactivations, after relatively short periods of operation, are therefore necessary in order to maintain the catalyst in an active state. Because of this, a plurality of reactors are preferably employed, each disposed within a separate heating or cooling zone, and in order to make the operation continuous, with respect to the balance of the equipment, the catalysts may be reactivated in some of the reactors while the catalysts in others are contacted with the process vapors. Although the type of reactor described above has been found to have many advantages when employed in this particular process, various other kinds of reactors may be employed without departing from the broad scope of the invention.

Catalysts are preferably employed which have been found to be highly efficient in the catalytic dehydrogenation of hydrocarbon oil vapors to produce optimum yields of olefinic liquid hydrocarbons. The preferred catalysts for effecting dehydrogenation are the catalysts consisting of activated aluminum oxide supporting chromium sesquioxide. Such catalysts are preferably produced by the deposition of chromium trioxide or its salt or salts of trivalent chromium, such as chromium nitrate, $Cr(NO_3)_3$, or by the precipitation of chromium trihydroxide, $Cr(OH)_3$ upon alumina granules.

While the present process has been found to operate very effectively in dehydrogenating hydrocarbon oils when employing an alumina-chromia catalyst, the process is not limited to this particular composition of catalyst but may employ other composite catalysts of a more or less refractory character, such as, for example, alumina or silica or an inert refractory material composited with compounds, and preferably the oxides selected from the group comprising compounds and oxides of the elements in the left hand columns of groups 4, 5, and 6 in the periodic table. The catalysts which are alternately utilizable are not exactly equivalent in their reaction and are not to be considered as absolute substitutes one for the other, which fact will be more or less apparent to those conversant with the practical aspects of catalysis.

In the case here illustrated, when the catalyst is reactivated the flow of hydrocarbon vapors is stopped and suitable reactivating gases at an elevated temperature containing regulated quantities of oxygen are introduced to reactor 10 by way of line 17, valve 18, and line 8. The reactivating gases pass through reactor tubes 11 and due to oxidation the carbon deposited upon the catalysts disposed therein is caused to burn and the resulting gases are discharged from reactor 10 by way of line 19, line 20, and valve 21 and may be recirculated or discharged to the atmosphere as desired. When reactivating, the reaction that takes place is exothermic, and, therefore, a suitable means must be employed to dissipate the heat. This may be accomplished by directing cooled combustion gases into reactor 14 by way of duct 15, passing the same in indirect heat exchange relationship with the reactivating gases in reactor tubes 11 and discharging them by way of duct 16.

The products of dehydrogenation from reactor 10 are directed through line 19 and valve 22 into cooler 23 wherein they are cooled to a temperature substantially below that at which pyrolytic cracking is effected. The cooled products of dehydrogenation from cooler 23 are directed through line 24 and valve 25 into separator and absorber 26. Fixed gases produced in the dehydrogenation reaction are preferably separated from the liquid products in separator and absorber 26. Provision is made for introducing cooled reflux condensate, produced as subsequently described, to the upper portion of separator and absorber 26 by way of line 89 as a cooling and refluxing medium therein and as an absorber oil for the lighter normally liquid hydrocarbons. Provision is also made for reboiling the bottoms of separator and absorber 26 by passing a suitable heating medium through closed coil 27.

Although separator and absorber 26 is preferably operated to remove all of the normally gaseous hydrocarbons, it may be desirable at times to separate only hydrogen and methane, in which case the balance of the normally gaseous hydrocarbons would be contained in the liquid recovered as bottoms in this step. In any case, the fixed gases separated in separator and absorber 26 are directed from the upper portion thereof through line 28 and valve 29 to cooling and storage or elsewhere as desired. The liquid products of dehydrogenation collected in the lower portion of separator and absorber 26, comprising normally liquid hydrocarbons and, when desired, condensed and dissolved normally gaseous hydrocarbons, are directed from the lower portion thereof through line 30 and valve 31 to pump 32 which discharged through line 33 and valve 34 into heating coil 35.

The products of dehydrogenation introduced to heating coil 35 are vaporized therein and raised to the desired reaction temperature, without substantial pyrolytic cracking thereof, by means of heat supplied from furnace 36. The heated vapors from heating coil 35 are directed through line 37 and valve 38 into catalytic reactor 39 and is contacted with a cracking catalyst suitably disposed therein.

Preferably and in the case here illustrated, reactor 39 comprises an apparatus of like design to reactor 10 consisting essentially of reactor tubes 40, upper and lower heaters 41 and 42, and disposed within heating or cooling zone 43. Catalytic cracking is also an endothermic reaction and, therefore, provision is made for the introduction and withdrawal of hot combustion gases to zone 43 during the processing cycle and for the introduction and withdrawal of cooler com-

bustion gases during the reactivating cycle, ducts 44 and 45 being supplied for this purpose.

When desired, steam may be introduced with the charge to reactor 39 in order to assist in vaporizing the charge and in reducing the effective pressure on the hydrocarbon vapors. Steam may be introduced to the products of dehydrogenation prior to their introduction to heating coil 35 by way of line 46 and valve 47, or after they have been vaporized in heating coil 35 by way of line 48 and valve 49.

Catalysts which have been found to be highly efficient in the catalytic cracking of hydrocarbon vapors consist in general of uniform size pellets of specially prepared silica composited with alumina, the amount of the alumina being varied to suit requirements depending upon the stock to be treated and the operating conditions employed. As a rough average, good results are usually obtained, for example, when employing silica composited with 15% alumina. This alumina percentage is varied for best results under specific conditions over a relatively wide range, for example, from 2% to 50%, or alumina may be employed as the major ingredient and the silica varied over substantially the same range as the alumina, i. e., 2% to 50%. Catalysts of this character may be initially prepared in any of several different manners and subsequently dried. The preferred catalyst is prepared by precipitating silica hydrogel from a solution of sodium silicate by acidifying with an acid, such as hydrochloric acid, for example, subsequently treating and washing the silica hydrogel to remove substantially all of the alkali metal ions, suspending the purified silica hydrogel in a solution of aluminum salts and depositing the alumina hydrogel upon the suspended silica by the addition of volatile basic precipitants, such as, for example, ammonium hydroxide, ammonium carbonate, or ammonium sulfide. After the alumina hydrogel has been deposited upon the purified silica hydrogel the material is dried, formed into pellets and calcined at a temperature of approximately 850 to 1000° F. The process, however, is not limited to this particular composition of cracking catalyst but may employ other composite catalysts of a refractory character, such as, for example, silica composited with compounds selected from the group consisting of zirconia, vanadia, alumina-zirconia or alumina-thoria, and other catalysts such as acid treated clays may be employed. The catalysts referred to above are not exactly equivalent in their reaction and are not to be considered as absolute substitutes one for the other, which fact will be more or less apparent to those conversant with the practical aspects of catalysis.

In catalytic cracking, as in dehydrogenation, the deposition of carbon on the active surface of the catalyst lowers its activity and, therefore, in order to obtain best results frequent reactivation of the catalyst is desirable. In order that this operation may be made continuous along with the rest of the process, a plurality of reactors are preferably employed each disposed within a separate heating or cooling zone in order that they may be separately processed and reactivated. Reactivation of the cracking catalyst is accomplished by burning the carbonaceous deposits from the catalyst in the presence of an oxygen-containing gas which is introduced to the reactor by way of line 50, valve 51, and line 37 and is discharged therefrom through line 52, line 53 and valve 54.

The conversion products from reactor 39 are directed through line 52 and valve 53, preferably cooled to a temperature below that at which substantial pyrolytic cracking is effected by commingling with the same a suitable cooling medium, introduced as subsequently described, and the conversion products, together with the cooling oil, are introduced to separating zone 57 within combined fractionator and separator 56. As illustrated in the accompanying drawing, vessel 56 comprises a separating zone 57 in its lower portion and a fractionating zone 58 separated from said separating zone by means of reflux trapout tray 59. However, other means may be employed to accomplish the same purpose, such as, for example, separate vessels.

In separating zone 57, the vaporous components are separated from the non-vaporous liquid residue which is directed through the lower portion thereof through line 60 and valve 61 to cooling and storage or elsewhere as desired. The vaporous components are subjected to fractionation in fractionating zone 58 to separate fractionated vapors in the gasoline boiling range from the higher boiling hydrocarbons.

Fractionated vapors of the desired end boiling point are directed from the upper portion of fractionating zone 58 through line 62 and valve 63 to cooler and condenser 64. The resulting gas-containing distillate, together with undissolved and uncondensed gases discharged from condenser 64, are directed through line 65 and valve 66 to receiver 67.

Undissolved and uncondensed gases collected and separated in receiver 67 are directed from the upper portion thereof through line 68 and valve 69 to collection and storage or elsewhere as desired. Regulated portions of the distillate collected and separated in receiver 67 are directed through line 70 and valve 71 to pump 72 which discharges through line 73 and valve 74 into the upper portion of fractionating zone 58 for refluxing and cooling therein. The remaining distillate collected and separated in receiver 67 is directed from the lower portion thereof through line 75 and valve 76 to stabilization and subsequent storage or elsewhere as desired. Water collected in the lower portion of receiver 67 resulting from the condensation of steam employed in the process is directed from the lower portion thereof through line 77 and valve 78 to waste.

The higher boiling hydrocarbons separated from the fractionated vapors, comprising a fraction whose average boiling point is above that of said fractionated vapors, are condensed as reflux condensate in fractionating zone 58 and collected on trapout tray 59. This reflux condensate withdrawn from the lower portion of fractionating zone 58 through line 79 may be directed through line 80 containing valve 81 to cooling and storage as a product of the process. Preferably, however, the reflux condensate is supplied to the catalytic cracking step to obtain substantial further conversion thereof. This may be accomplished by directing the reflux condensate in line 79 through valve 82 to pump 83. Pump 83 discharges through line 84 and a portion of the reflux condensate is directed through line 85 and valve 86 into line 52, commingling therein with the conversion products discharged from reactor 39 in order to cool said conversion products, as previously described. The balance of the reflux condensate in line 84 may be directed all or in part through line 93

and valve 87 to sub-cooler 88. The cooled reflux condensate is discharged from sub-cooler 88 through line 89 containing valve 90 into the upper portion of separator and absorber 26 to act as a cooling and absorption medium, as previously described. On the other hand, instead of introducing all of the balance of the reflux condensate to separator and absorber 26 as an absorption oil, all or a portion of this quantity in line 84 may be directed through line 91 and valve 92 into line 33 for conversion in commingled state with the liquid products of dehydrogenation or a portion may be returned to the dehydrogenation step by directing it through valve 94 into line 4.

The preferred range of operating conditions which may be employed in an apparatus such as illustrated and above described to accomplish the desired results is approximately as follows:

The heater to which the charging stock is supplied may employ an outlet temperature ranging, for example, from 800 to 1200° F. and a superatmospheric pressure of from approximately 20 to 100 pounds or more per square inch. Substantially the same conditions of temperature and pressure are maintained on the process vapors introduced to the catalytic dehydrogenation reactor as are employed on the outlet of the heating coil to which the charging stock is supplied. The separator and absorber may employ a superatmospheric pressure substantially the same as that on the outlet of the catalytic dehydrogenation reactor. The furnace to which the dehydrogenated products are introduced may employ an outlet temperature ranging, for example, from 800 to 1200° F. and a superatmospheric pressure of from 20 to 100 pounds or more per square inch. However, this process permits the utilization of lower temperatures than would otherwise be employed if the cracking step was not preceded by the dehydrogenation step. Substantially the same conditions of temperature and pressure may be utilized on the process vapors introduced to the catalytic cracking reactor as are employed on the outlet of the heating coil to which the dehydrogenated products are supplied. The conversion products discharged from the catalytic cracking reactor are preferably cooled to a temperature ranging, for example, from 600 to 800° F. or at least to a temperature below that at which substantial pyrolytic cracking is effected. The combined fractionator and separator may utilize a pressure substantially the same as that employed at the outlet of the catalytic cracking reactor.

I claim as my invention:

1. A process for treating paraffinic gasoline fractions which comprises contacting the paraffinic oil in a first stage with a dehydrogenating catalyst under dehydrogenating conditions, said catalyst and conditions being such as to convert the oil into a predominantly olefinic product, and subjecting said olefinic product in a second stage to cracking in the presence of a cracking catalyst of different composition than said dehydrogenating catalyst and which is selective in the breaking of carbon-to-carbon bonds.

2. A process for increasing the anti-knock value of paraffinic gasoline fractions which comprises dehydrogenating the paraffinic oil in a first stage in the presence of a dehydrogenating catalyst and under dehydrogenating conditions such as to convert the oil into a predominantly olefinic product, and subjecting said olefinic product in a second stage to catalytic cracking in the presence of a cracking catalyst of different composition than said dehydrogenating catalyst.

3. The process as defined in claim 1 further characterized in that said dehydrogenating catalyst comprises an alumina-chromia composite and said cracking catalyst predominates in silica.

4. The process as defined in claim 1 further characterized in that said cracking catalyst comprises a silica-alumina composite.

5. The process as defined in claim 1 further characterized in that said cracking catalyst comprises a silica-zirconia composite.

6. The process as defined in claim 2 further characterized in that said dehydrogenating catalyst comprises an alumina-chromia composite and said cracking catalyst predominates in silica.

7. The process as defined in claim 2 further characterized in that said cracking catalyst comprises a silica-alumina composite.

8. The process as defined in claim 2 further characterized in that said cracking catalyst comprises a silica-zirconia composite.

9. A process for increasing the anti-knock value of paraffinic gasoline fractions which comprises dehydrogenating the paraffinic oil in a first stage in the presence of an alumina-chromia catalyst under dehydrogenating conditions such as to convert the oil into a predominantly olefinic product, and subjecting said olefin product in a second stage to catalytic cracking in the presence of a silica-alumina composite.

10. A process for increasing the anti-knock value of paraffinic gasoline fractions which comprises dehydrogenating the paraffinic oil in a first stage in the presence of an alumina-chromia catalyst under dehydrogenating conditions such as to convert the oil into a predominantly olefinic product, and subjecting said olefin product in a second stage to catalytic cracking in the presence of a silica-zirconia composite.

11. The process as defined in claim 1 further characterized in that said cracking catalyst comprises silica, alumina and zirconia.

12. The process as defined in claim 9 further characterized in that said composite contains zirconia in addition to the silica and alumina.

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