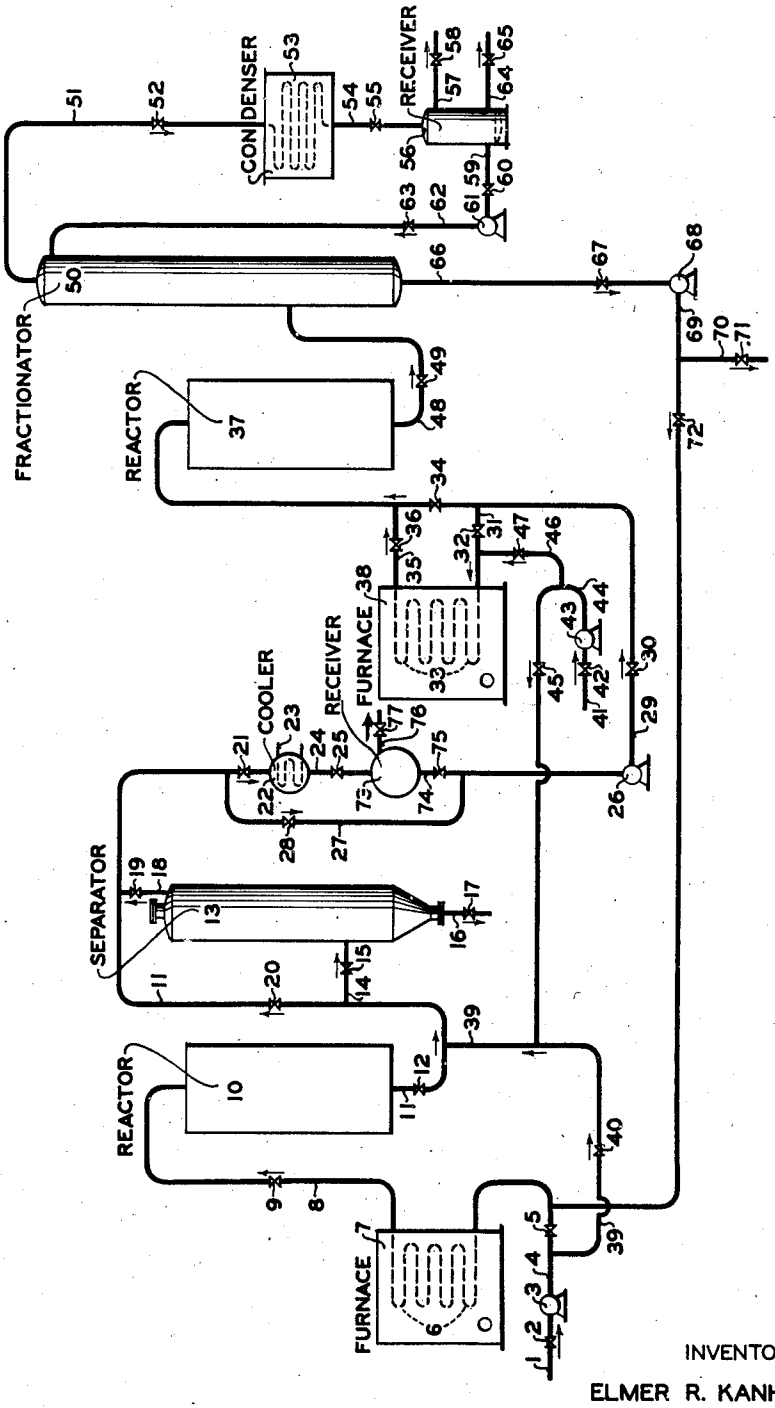
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HYDROCARBON CONVERSION

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HYDROCARBON CONVERSION

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This invention relates to a process which involves a series of concomitant steps wherein hydrocarbon oils are converted into substantial yields of high actane rating gasoline having a relatively low olefin content and improved properties with respect to susceptibility to antiknocking agents and, in addition, improved storage stability and low sulfur content.

The invention involves principally high temperature catalytic cracking treatment of a hydrocarbon oil, low temperature catalytic cracking treatment of the conversion products from the high temperature cracking zone in the presence of an added saturated hydrocarbon oil, separation of the low temperature conversion products to separate the gasoline boiling range hydrocarbons from the higher boiling hydrocarbons, recovery of the former, and the return of the latter to the high temperature cracking zone.

The term "high temperature catalytic cracking treatment" as used throughout the specification and claims refers to the treatment of a hydrocarbon oil boiling above the range of gasoline in the presence of a cracking catalyst at a temperature in the range of from 800 to 1200° F. and at a pressure ranging, for example, from substantially atmospheric to 200 pounds or more per square inch whereby to effect substantial conversion into gasoline boiling range hydrocarbons and/or to the treatment of gasoline boiling range hydrocarbons to improve the properties of the same by changing their structure without materially altering their boiling range; whereas low temperature catalytic cracking treatment refers to the treatment of a mixture of hydrocarbon oil containing the cracked conversion products from the high temperature cracking treatment and an added saturated hydrocarbon oil in the presence of a cracking catalyst at a temperature in the range of 500 to 800° F., but preferably from 700 to 800° F., and at a pressure ranging, for example, from substantially atmospheric to 200 pounds or more per square inch whereby to increase the degree of saturation of the olefinic hydrocarbons subjected to treatment and at the same time effect some cracking of the heavier hydrocarbons.

In one specific embodiment the invention comprises passing hydrocarbon oil in the heated vaporous state in contact with a catalyst mass in a high temperature cracking zone whereby to effect substantial conversion to gasoline, cooling the conversion products, separating a non-vaporous liquid residue from the vaporous conversion products, recovering the former, commingling said vaporous conversion products with an added saturated hydrocarbon oil and passing the mixture in the heated state in contact with a catalyst mass in a low temperature cracking zone whereby to increase the degree of saturation of the olefinic hydrocarbons contained in the mixture in addition to cracking some of the heavier hydrocarbons, fractionating the conversion products from the low temperature cracking zone to separate fractionated vapors boiling in the range of gasoline from the higher boiling hydrocarbons, recovering the former, condensing the latter in the fractionating zone as reflux condensate, and returning it to the high temperature cracking zone.

In the catalytic cracking processes now in use, it is common to employ relatively high temperatures and relatively short contact times in order to obtain a substantial rate of conversion of the hydrocarbon oil to gasoline boiling range hydrocarbons. However, the gasoline obtained from such a process contains high percentages of olefinic hydrocarbons which, although increasing the octane rating of the gasoline, are responsible for the poorer susceptibility of the gasoline to added antiknocking agents, such as tetraethyl lead, and, in addition, are responsible for the poorer storage stability because of gum formation. It has been found that if the vaporous conversion products from the high temperature cracking treatment are commingled with a saturated straight-run hydrocarbon oil and the mixture subjected to contact with a catalyst mass of essentially the same composition as that employed in the high temperature cracking treatment and at a temperature in the range of 500 to 800° F. for a relatively longer period of time than that employed in the preceding cracking treatment, a gasoline product is obtained composed primarily of paraffinic and aromatic hydrocarbons which have a relatively high octane rating, a low potential gum content, and a good susceptibility to antiknocking agents whereby it is possible with the addition of relatively small amounts of tetraethyl lead to obtain a gasoline suitable for aviation purposes.

It is believed that in the low temperature catalytic cracking, as described above, that a portion of the hydrogen from the saturated hydrocarbons and particularly the naphthenic hydrocarbons is transferred to the olefinic hydrocarbons formed in the high temperature cracking treatment, whereby the olefinic hydrocarbons become saturated to form paraffinic hydrocarbons and the naphthenic hydrocarbons converted to aro-

matic hydrocarbons. Various other reactions, such as, for example, dehydrogenation and cyclization of an aliphatic hydrocarbon to form an aromatic hydrocarbon with the formation of 2 to 3 molecules of hydrogen which attach to the unreacted olefinic hydrocarbons, may also take place. A further discussion in connection with what may possibly take place is unnecessary, since the invention does not concern itself with the chemistry of the various reactions but is concerned primarily with the process in which the cracking reaction may be conducted.

The accompanying diagrammatic drawing shows in conventional side elevation one specific form of the apparatus in which the object of the invention may be accomplished. It is to be understood that the invention is not limited to processing in the specific form of apparatus herein disclosed and that various modifications of the process and apparatus herein described may be made without departing from the broad scope of the invention.

Referring now to the drawing, the charging stock comprising either a relatively wide boiling range hydrocarbon oil, which may be substantially completely vaporized, or any fraction thereof, is introduced through line 1 and valve 2 to pump 3, which discharges through line 4 and valve 5. The charging stock is commingled in line 4 with cycle stock, formed as hereinafter described, and the mixture introduced to heating coil 6. The oil in passing through heating coil 6 is substantially completely vaporized therein and raised to the desired temperature, which may range, for example, from 800 to 1200° F., without substantial pyrolytic cracking thereof by means of heat supplied from furnace 7. The heated hydrocarbon vapors leaving heating coil 6 at a pressure ranging, for example, from substantially atmospheric to 200 pounds or more per square inch, are directed through line 8 and valve 9 into reactor 10 wherein the vapors are subjected to contact with a cracking catalyst disposed therein while maintaining the hydrocarbon vapors at substantially the same temperature as that employed on the outlet of the heating coil whereby to effect substantial conversion of the gasoline boiling range hydrocarbons.

The preferred cracking catalysts for use in the present process consist in general of a precipitated alumina hydrogel and/or zirconia hydrogel composited with silica hydrogel, the gel composite being washed, dried, formed into particles and calcined to produce a catalytic mass. It is not intended, however, that the process should be limited to these particular catalysts, for other catalysts, such as, for example, the hydrosilicates of alumina, acid treated clays, and the like, may be used within the broad scope of the invention.

In the following specification and claims the terms silica, alumina, silica-zirconia, and silica-alumina-zirconia masses are used in the broad sense to designate the synthetic composites referred to above. The preferred catalysts may be prepared by precipitating silica from a solution as a hydrogel within or upon which the alumina and/or zirconia are deposited also by precipitation as hydrogels. The silica hydrogel may conveniently be prepared by acidifying an aqueous solution of sodium silicate by the addition of a required amount of hydrochloric acid. After precipitating, the silica gel is preferably washed until substantially free from alkali metal salts. The washed silica hydrogel is then suspended in a solution of alumina and/or zirconium salts and an alkaline precipitant, such as ammonium hydroxide, ammonium carbonate or ammonium sulfide added to the solution to precipitate aluminum and/or zirconium hydrogels. The final precipitate, comprising essentially hydrated silica and hydrated alumina and/or zirconia, is washed to substantially completely remove water soluble materials and dried at about 300° F. to produce a rather crumbly and granular material which may be ground and pelleted or sized to produce particles of catalyst after which the catalyst particles are calcined at a temperature in the approximate range of 1000 to 1500° F. Various other procedures, such as, for example, coprecipitation of the hydrated gels may be employed, when desired, to produce the preferred catalyst.

Reactor 10 is preferably of the type which employs a plurality of relatively small diameter reactor tubes containing the desired catalyst, the tubes being confined within an enclosed zone to which heat from an external source may be supplied for the purpose of maintaining the reactants at the desired temperature during the conversion reaction. In addition, since relatively short periods of operation are employed in catalytic cracking because of the rather rapid deposition of carbon upon the surface and within the pores of the catalyst particles which necessitates frequent reactivation, it is preferred that a plurality of reactors be employed, although only one is shown in the drawing, in order that one or more may be segregated and the catalysts disposed therein subjected to reactivation while conversion of the hydrocarbon vapors is being accomplished in the other or others. Suitable means, not shown, may be employed for reactivating the catalyst disposed within the various reactors during the period those particular reactors are segregated from the balance for the purpose of reactivation.

Although the reactor described above constitutes the preferred type of reactor, it is not intended that the invention should be limited in this respect, for various other types of reactors, known to those in the art, may be substituted therefor without departing from the broad scope of the invention.

The conversion products leaving reactor 10 are directed through line 11 and valve 12, preferably commingled with a saturated hydrocarbon oil, introduced as hereinafter described, in order to cool the conversion products, and the mixture introduced to separator 13 by way of line 14 and valve 15 to separate a non-vaporous liquid residue from the vaporous hydrocarbons. The non-vaporous liquid residue may be removed from separator 13 by way of line 16 and valve 17, cooled and recovered as a product of the process, in which case the vaporous hydrocarbons are directed into line 11 by way of line 18 and valve 19 and treated as subsequently described. However, when the conversion products contain little or no non-vaporous liquid residue, separator 13 may be by-passed by closing valves 15 and 19 in lines 14 and 18, respectively, and the conversion products, either alone or in commingled state with an added saturated hydrocarbon oil, are directed through valve 20.

In any case, the conversion products, either alone or in commingled state with the added saturated hydrocarbon oil in line 11, are supplied to pump 26, either in the vapor state, or, when desired, as a normally liquid hydrocarbon. The vapors in line 11 may, when desired, be directed

through line 27 and valve 28 into line 74 by means of which they are supplied to pump 26.

In the above procedure, a vapor pump would ordinarily be necessary since the pressure on the hydrocarbon vapors in line 11 is below the desired pressure for use in the subsequent treatment. The preferred method is to cool and condense the vapors in line 11, separate the normally gaseous hydrocarbons from the normally liquid hydrocarbons and utilize only the normally liquid hydrocarbons. This may be accomplished by directing the vapors in line 11 through valve 21 into cooler 22 wherein indirect heat exchange is effected between the vapors and the cooling medium, supplied to cooler 22 by way of closed coil 23. The cooled mixture leaving cooler 22 is directed through line 24 and valve 25 into receiver 73 wherein the normally liquid and normally gaseous hydrocarbons are collected and separated. The normally gaseous hydrocarbons are withdrawn through line 76 and valve 77 and recovered. The normally liquid hydrocarbons are directed through line 74 and valve 75 to pump 26. Pump 26 discharges the oil and/or vapors through line 29 and valve 30 and a portion or all may be directed through line 31 and valve 32 into heating coil 33, or, when desired, the hydrocarbons may be directed through valve 34 into reactor 37. When the saturated oil is commingled with the conversion products for the purpose of cooling, the temperature of the mixture determines whether additional heat is necessary in heating coil 33. For example, if the temperature of the mixture is below that at which the conversion in reactor 37 is to be effected, the hydrocarbons are directed through line 31 and valve 32 into heating coil 33 wherein they are raised to the desired temperature, which may range, for example, from 500 to 800° F., and preferably from 700 to 800° F., by means of heat supplied from furnace 38. The oil after being raised to the desired temperature in heating coil 33 is returned to line 29 by way of line 35 and valve 36.

A saturated hydrocarbon oil, which is used as the hydrogen donor in the subsequent low temperature cracking zone, is preferably employed as the cooling oil for the conversion products in line 11 and may comprise, for example, a portion of the hydrocarbon oil subjected to conversion in the high temperature catalytic cracking treatment or a straight-run gasoline, naphtha or kerosene. The purpose, of course, in employing a saturated hydrocarbon oil as a cooling oil is due to the fact that whatever oil is employed, it eventually finds its way into the low temperature cracking zone, and if recycle stock were to be employed as the cooling oil, very little, if anything, would be gained because it contains the hydrocarbons which have already acted as hydrogen donors. In addition, if the cycle stock is employed as the cooling medium, it merely necessitates the use of a larger reactor in the low temperature catalytic cracking treatment, because in such a case it would also be necessary to add sufficient quantities of straight-run hydrocarbon oil to serve as a hydrogen donor, whereas if the straight-run hydrocarbon oil was used directly as the cooling medium only it and the conversion products from the high temperature cracking treatment would be subjected to the low temperature cracking treatment.

If the same oil that is charged to the high temperature cracking treatment is employed as a cooling medium to the conversion products in line 11, a portion of the same in line 4 may be directed through line 39 and valve 40 into line 11. On the other hand, when it is desired to use straight-run gasoline, naphtha or kerosene, this may be supplied by way of line 41, valve 42, pump 43, line 44, valve 45, and line 39. In addition, when the amount of cooling oil added to the conversion products in line 11 is insufficient to serve as a hydrogen donor to the conversion products subjected to low temperature cracking treatment, additional quantities of the gasoline, naphtha or kerosene in line 44 may be supplied to the process by way of line 46 and valve 47 whereby it either commingles with the mixture of conversion products and cooling oil in line 31 after which it is introduced to heating coil 33, or supplied alone to heating coil 33 by way of line 31.

In any case, the mixture of conversion products and added saturated hydrocarbon oil in line 29, ranging in temperature from 500 to 800° F. and at a pressure ranging, for example, from substantially atmospheric to 200 pounds or more per square inch, are introduced to reactor 37 wherein they are subjected to contact with a catalyst disposed therein. The catalyst employed in reactor 37 is of essentially the same composition as that described in connection with the catalyst employed in reactor 10. The low and high temperature catalytic cracking reactions differ essentially with respect to temperatures and contact times employed, the reaction in reactor 10 being carried out at a relatively high temperature and short contact time, whereas the reaction in reactor 37 is carried out at a lower temperature and at a longer contact time. Reactor 37 and 10 may be of essentially the same design, however, as was previously mentioned. Various other types of reactors may be employed to accomplish the desired results.

The conversion products leaving reactor 37 are directed through line 48 and valve 49 to fractionator 50 wherein fractionated vapors boiling in the range of gasoline are separated from the higher boiling hydrocarbons, the latter being condensed as reflux condensate in the fractionating zone. The fractionated vapors are directed from the upper portion of fractionator 50 through line 51 and valve 52 to cooler and condenser 53. Distillate leaving condenser 53, together with undissolved and uncondensed gases, is directed through line 54 and valve 55 into receiver 56 wherein the undissolved and uncondensed gases are separated from the distillate. The gases separated in receiver 56 are directed from the upper portion thereof through line 57 and valve 58 to storage or disposed of in any suitable manner. A portion of the distillate collected in the lower portion of receiver 56 is returned to the upper portion of fractionator 50 as a refluxing and cooling medium therein by way of line 59, valve 60, pump 61, line 62, and valve 63. The balance of the distillate collected in receiver 56 is directed through line 64 and valve 65 to storage or to further treatment as desired.

The reflux condensate from fractionator 50 is directed through line 66 and valve 67 to pump 68. Pump 68 discharges through line 69 and all or a portion of the reflux condensate may be directed through line 70 and valve 71, cooled and recovered as a product of the process. Preferably, however, it is directed through valve 72 into line 4 where it commingles with the charging stock and is subjected to conversion, as previously described.

An example of one specific operation of the process as it may be accomplished in an appara-

tus such as illustrated and above described to accomplish the desired results is approximately as follows:

A 30.7° A. P. I. gravity East Texas gas-oil was vaporized and heated to a temperature of approximately 932° F. without substantial pyrolytic cracking thereof. The heated vapors under a superatmospheric pressure of approximately 60 pounds per square inch were passed over a silica-alumina-zirconia catalyst at a liquid space velocity of 4 while maintaining the temperature of the vapors at approximately that at which they were discharged from the heater. The conversion products leaving the catalyst zone were cooled to a temperature of approximately 650° F. with a portion of the gas-oil charging stock and the mixture introduced to a separator maintained under a superatmospheric pressure of approximately 40 pounds per square inch wherein the non-vaporous liquid residue was separated from the vaporous conversion products. The non-vaporous liquid residue removed from this zone was cooled and recovered as a product of the process. The vaporous conversion products leaving the separator were subjected to cooling and condensation. The resulting cooled and condensed conversion products and cooling oil existing in the proportion of approximately 3:1, respectively, were heated to a temperature of 750° F. and the heated oil passed over a silica-alumina-zirconia catalyst at a liquid space velocity of 1 and at a superatmospheric pressure of approximately 60 pounds per square inch while maintaining the temperature substantially constant during the conversion reaction. The conversion products leaving the low temperaturature cracking zone were subjected to fractionation at a superatmospheric pressure of approximately 40 pounds per square inch to separate fractionated vapors having an end boiling point of approximately 300° F. from the higher boiling conversion products, the latter being condensed as reflux condensate in this zone and returned to the high temperature cracking treatment. The fractionated vapors were subjected to cooling and condensation and the resulting distillate and gas collected and separated.

When employing an operating period of 1 hour before regeneration of the catalyst in the high temperature cracking treatment and ½ hour before regeneration of the catalyst in the low temperature cracking treatment, approximately 55% by volume of 300 end point gasoline was obtained having a bromine number of 10 and an octane rating of 80 which was raised to 96 upon the addition of 6 cc. of tetraethyl lead.

I claim as my invention:

1. A process for producing motor fuel of high octane rating and relatively low olefin content which comprises subjecting hydrocarbon oil to catalytic cracking at a temperature in the approximate range of 800 to 1200° F. for a contact time such as to form olefinic gasoline, commingling a saturated hydrocarbon oil with the resultant olefinic gasoline products and contacting the mixture with a cracking catalyst at a temperature in the approximate range of 500 to 800° F. for a longer contact time than is employed in the first-mentioned catalytic step, the quantity of said saturated oil and said longer contact time being sufficient to saturate at least the major portion of the olefin content of said gasoline products, and recovering the thus saturated, catalytically cracked gasoline.

2. A process for producing motor fuel of high octane rating and relatively low olefin content which comprises subjecting hydrocarbon oil to catalytic cracking at a temperature in the approximate range of 800 to 1200° F. for a contact time such as to form olefinic gasoline, commingling a saturated hydrocarbon oil with the resultant olefinic gasoline products and contacting the mixture with a cracking catalyst at a temperature in the approximate range of 500 to 800° F. for a longer contact time than is employed in the first-mentioned catalytic step, the quantity of said saturated oil and said longer contact time being sufficient to saturate at least the major portion of the olefin content of said gasoline products, separating the thus saturated, catalytically cracked gasoline from fractions heavier than gasoline and returning at least a portion of the latter to the first-mentioned catalytic cracking step.

3. The process as defined in claim 1 further characterized in that said saturated oil is commingled with the heated conversion products of said catalytic cracking whereby to cool these products.

4. The process as defined in claim 1 further characterized in that said saturated oil comprises a straight-run petroleum product.

5. A process for producing motor fuel of high octane rating and relatively low olefin content from a saturated hydrocarbon charging oil heavier than gasoline, which comprises subjecting a portion of said charging oil to catalytic cracking at a temperature in the approximate range of 800 to 1200° F., commingling with the resultant olefinic gasoline products another portion of the saturated charging oil and contacting the mixture with a cracking catalyst at a temperature in the approximate range of 500 to 800° F., the quantity of saturated charging oil so commingled and the contact time of the mixture with said cracking catalyst being sufficient to saturate at least the major portion of the olefin content of said gasoline products, and recovering the thus saturated, catalytically cracked gasoline.

6. The process as defined in claim 1 further characterized in that said mixture is contacted with the cracking catalyst at a temperature of about 700 to 800° F.

7. The process as defined in claim 5 further characterized in that said mixture is contacted with the cracking catalyst at a temperature of about 700 to 800° F.

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