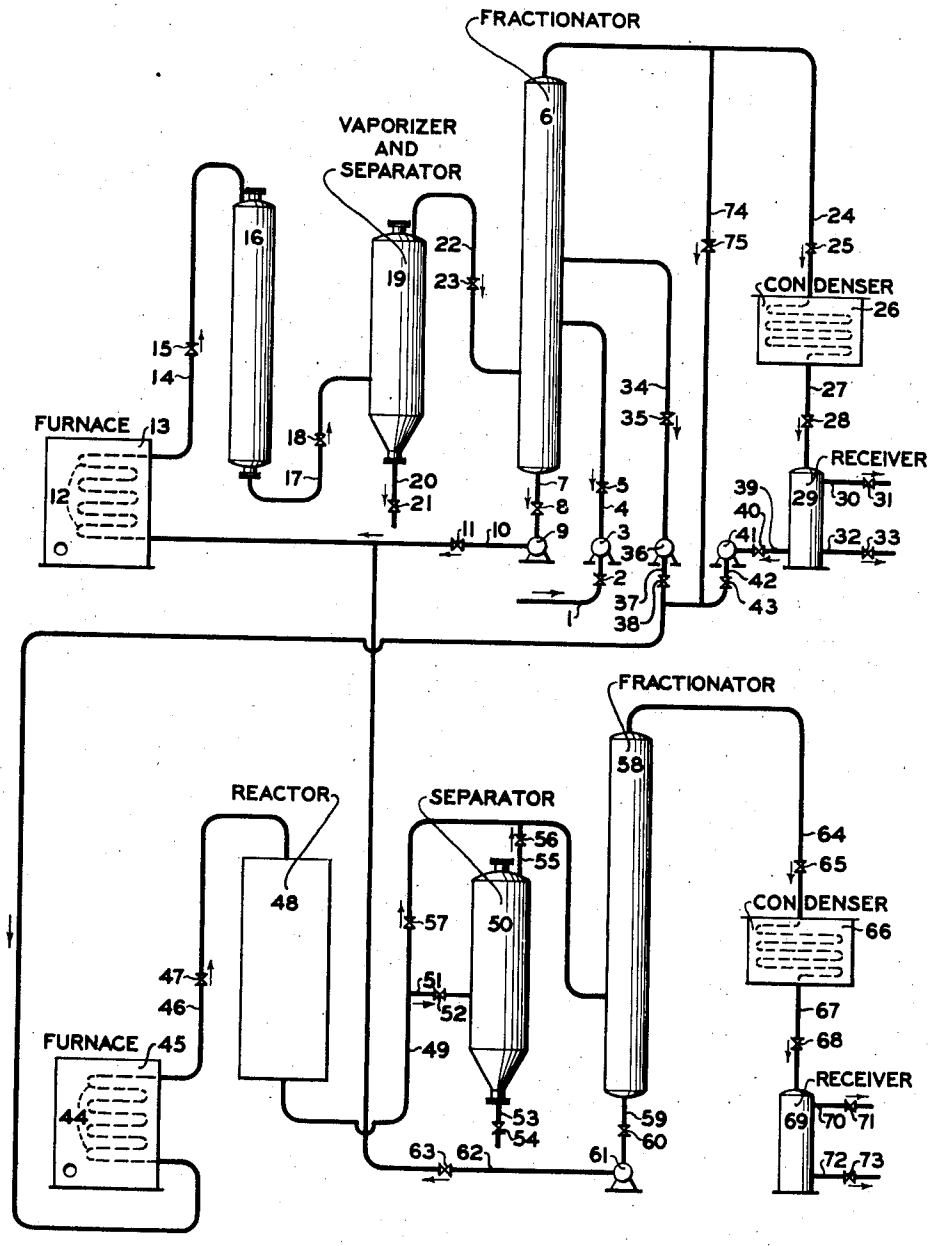
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HYDROCARBON CONVERSION

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INVENTOR

ELMER R. KANHOFER

BY Lee Parry

ATTORNEY

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HYDROCARBON CONVERSION

Elmer R. Kanhofer, Chicago, Ill., assignor to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

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This invention relates to a process which involves a series of concomitant steps wherein the hydrocarbon oils are converted into substantial yields of high octane 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 thermal cracking of combined feed formed in the fractionator of a thermal cracking step, low temperature catalytic cracking treatment of the thermally cracked gasoline and/or the light recycle from the thermal cracking treatment, together with a saturated hydrocarbon oil, the mixture of the saturated and cracked hydrocarbon oil being formed in the fractionator of the thermal cracking step, fractionation of the conversion products from the low temperature catalytic cracking treatment to separate the gasoline boiling range hydrocarbons from the higher boiling hydrocarbons, recovery of the former, and the return of the latter to the thermal cracking treatment.

The term "thermal cracking" as used throughout the specification and claims refers to the treatment of a hydrocarbon oil boiling above the range of gasoline under elevated temperatures and pressures whereby to effect substantial conversion into gasoline boiling range hydrocarbons. The term "low temperature catalytic cracking treatment" refers to the treatment of a mixture of saturated and unsaturated hydrocarbon oils 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 gasoline boiling range olefinic hydrocarbons subjected to treatment and at the same time effect some cracking of the heavier hydrocarbons.

In one specific embodiment the invention comprises fractionating a hydrocarbon oil charging stock in commingled state with thermally cracked vaporous conversion products, formed as hereinafter described, to separate fractionated vapors boiling in the range of gasoline from the higher boiling hydrocarbons, the latter being condensed in the fractionating zone as light and heavy combined feeds, subjecting the heavy combined feed to thermal cracking treatment in a heating coil and communicating reaction chamber, passing the resultant conversion products to a vaporizer and separator whereby to separate a non-vaporous liquid residue from the vaporous conversion products and the vapors formed within this zone, recovering said non-vaporous liquid residue, supplying said vaporous conversion products, together with the vapors formed in said vaporizer and separator to the fractionating zone, for treatment as previously described, condensing and collecting said fractionated vapors, supplying the condensed distillate, together with a light combined feed recovered as an intermediate fraction, to a low temperature catalytic cracking treatment, fractionating the conversion products from said low temperature catalytic cracking treatment 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 supplying it to the thermal cracking treatment for conversion in commingled state with said heavy combined feed.

In the thermal cracking treatment gasoline is produced which contains high percentages of olefinic hydrocarbons which, although tending to increase the octane rating of the same, 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 as compared to a gasoline which is predominantly paraffinic and/or aromatic in character. It has been found that if the gasoline and the light recycle produced in the thermal cracking treatment is commingled with a saturated hydrocarbon oil and the mixture subjected to contact with a catalyst mass of the type to be described more fully later, at a temperature in the range of 500 to 800° F. for a longer period of time than that ordinarily employed in catalytic cracking treatments, a gasoline product composed primarily of paraffinic and aromatic hydrocarbons is obtained which has a relatively high octance rating, low potential gum content, and good suscepibility 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 treatment, 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 thermal cracking treatment, whereby the olefinic hydrocarbons become saturated to form paraffinic hydrocarbons and

the naphthenic hydrocarbons are converted to aromatic 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 with the process for producing the desired result.

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, charging stock for the process, preferably comprising a wide boiling range hydrocarbon oil, such as crude oil or reduced crude, is introduced through line 1 and valve 2 to pump 3, which discharges through line 4 and valve 5 into fractionator 6, which preferably operates under a superatmospheric pressure ranging, for example, from 25 to 200 pounds or more per square inch. The hydrocarbon oil charging stock introduced to this zone is commingled with the vaporous conversion products, formed as hereinafter described, and the mixture fractionated to separate a light vaporous fraction consisting essentially of gasoline boiling range hydrocarbons from the higher boiling hydrocarbons, the latter being condensed in the fractionating zone to form light and heavy combined feeds consisting essentially of mixtures of conversion products and charging stock.

The heavy combined feed fraction collected in the lower portion of fractionator 6 is directed through line 7 and valve 8 to pump 9, which discharges through line 10 and valve 11. The combined feed is commingled with the reflux condensate formed in the subsequent low temperature catalytic cracking treatment, as hereinafter described, and the mixture introduced to heating coil 12. The oil in passing through heating coil 12 is subjected to a cracking temperature ranging, for example, from 850 to 1000° F. by means of heat supplied from furnace 13. The heated oil is discharged from heating coil 12 under a superatmospheric pressure ranging, for example, from 200 to 600 pounds or more per square inch and is directed through line 14 and valve 15 into reaction chamber 16 wherein the oil is subjected to prolonged conversion in passing therethrough.

Reaction chamber 16 is preferably maintained at substantially the same pressure as that employed in the outlet of heating coil 12 and is preferably insulated to reduce radiation losses therefrom although no insulation is shown in the drawing.

The vaporous and liquid conversion products leaving reaction chamber 16 are directed through line 17 and valve 18 into vaporizer and separator 19. Valve 18 is preferably a pressure control valve by means of which a substantial atmospheric pressure is maintained in heating coil 12 and communicating reaction chamber 16 and in addition permits a substantial reduction in pressure on the downstream side of the valve.

Vaporizer and separator 19 is preferably maintained at a substantially reduced pressure relative to that employed in reaction chamber 16 and may range, for example, from 25 to 200 pounds or more per square inch whereby the liquid conversion products introduced thereto undergo substantial further vaporization to form a non-vaporous liquid residue. The non-vaporous liquid residue is withdrawn from vaporizer and separator 19 by way of line 20 and valve 21, cooled and recovered as a product of the process. The vaporous conversion products, together with the vapors evolved in vaporizer and separator 19 are directed through line 22 and valve 23 into fractionator 6, for treatment as previously described.

The light vaporous fraction from fractionator 6 is directed through line 24 and valve 25 to cooler and condenser 26 wherein the normally liquid hydrocarbons are condensed to form a distillate. The distillate, together with the undissolved and uncondensed gases leaving condenser 26 is directed through line 27 and valve 28 to receiver 29 wherein the distillate and gases are collected and separated. The normally gaseous hydrocarbons collected and separated in receiver 29 are directed through line 30 and valve 31 to storage or to further treatment as desired. A portion of the distillate collected and separated in receiver 29 may be returned to the upper portion of fractionator 6, by well known means not shown, for refluxing and cooling the upper portion thereof. When desired, a portion or all of the distillate collected in receiver 29 not employed as a refluxing medium in fractionator 6 may be recovered as a product of the process by withdrawing the same through line 32 and valve 33 from receiver 29. However, the preferred treatment, in accordance with the objects of the invention, is to treat the distillate fraction in the presence of a catalyst whereby to effect a substantial degree of saturation of the olefinic hydrocarbons contained therein, in the manner described as hereinafter set forth. When desired, instead of condensing all of the fractionated vapors, only the quantity necessary for use as a refluxing medium may be condensed and the balance, including gases from the cracking, directed through line 74 and valve 75 into line 42 for treatment as subsequently described.

The distillate fraction from the above described operation will ordinarily contain both cracked and straight-run gasoline boiling range hydrocarbons, which after treatment in the presence of a catalyst mass, of the type to be described, yield a product which is predominantly paraffinic and aromatic in character. However, since the light recycle stock from the thermal cracking treatment has a high potential gasoline content and since this light combined feed fraction from the above described operation contains both cracked and straight-run hydrocarbons, it is preferred that this fraction also be subjected to low temperature catalytic cracking treatment to produce additional gasoline therefrom. In addition, since the operating conditions for treating both the distillate and light combined feed fractions are essentially the same, the treatment of both fractions may be carried out in the same zone.

The light combined feed fraction from fractionator 6 is directed through line 34 and valve 35 to pump 36, which discharges through line 37 and valve 38 after which it commingles with the distillate fraction from receiver 29 having been

removed therefrom by way of line 39, valve 40, pump 41, line 42, and valve 43, or with the fractionated vapors introduced to line 14 as previously described. This mixture or either fraction alone is directed through line 37 to heating coil 44. The oil in passing through heating coil 44 is raised to the desired temperature which may range, for example, from 500 to 800° F. by means of heat supplied from furnace 45. The heated oil in leaving heating coil 44 at a pressure ranging, for example, from substantially atmospheric to 200 pounds or more per square inch is directed through line 46 and valve 47 into reactor 48 wherein it is subjected to contact with a cracking catalyst disposed therein while the temperature within the cracking zone is maintained at substantially the same temperature as that employed on the outlet of the heating coil whereby to reduce to a substantial degree the amount of olefinic hydrocarbons present in the feed introduced thereto and to effect some cracking of the higher boiling 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, co-precipitation of the hydrated gels may be employed, when desired, to produce the preferred catalyst.

Reactor 48 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 48 are directed through line 49, and when they contain non-vaporous liquid residue they may be introduced to separator 50 by way of line 51 and valve 52 wherein said non-vaporous liquid residue is removed from the vaporous conversion products and the former withdrawn from separator 50 by way of line 53 and valve 54 and recovered as a product of the process. The vaporous conversion products, in this case, are directed through line 55 and valve 56 into line 49. However, when the conversion products contain little or no non-vaporous liquid residue, separator 50 may be bypassed by closing valves 52 and 56 in lines 51 and 55, respectively, and the conversion products in line 49 directed through valve 57. In any case, the conversion products in line 49 are introduced to fractionator 58 wherein fractionated vapors boiling in the range of gasoline are separated from the higher boiling hydrocarbons, the latter being condensed as reflux condensate in this zone. The reflux condensate collected in fractionator 58 is directed through line 59 and valve 60 to pump 61, which discharges through line 62 and valve 63 into line 10 where it commingles with the combined feed from fractionator 6. It is thereafter subjected to conversion in heating coil 12, as previously described. The fractionated vapors are directed from the upper portion of fractionator 58 through line 64 and valve 65 to cooler and condenser 66. The distillate leaving condenser 66, together with undissolved and uncondensed gases, is directed through line 67 and valve 68 into receiver 69 wherein the undissolved and uncondensed gases are separated from the distillate. The gases collected and separated in receiver 69 are directed from the upper portion thereof through line 70 and valve 71 to storage or, when desired, to further treatment. A portion of the distillate collected in the lower portion of receiver 69 is returned to the upper portion of fractionator 58, by well known means not shown, as a refluxing and cooling medium therein. The balance of the distillate collected in receiver 69, containing predominantly paraffinic and aromatic hydrocarbons, is directed through line 72 and valve 73 to storage or to further treatment as desired.

An example of one specific operation of the process as it may be accomplished in an apparatus such as illustrated and above described to accomplish the desired results is approximately as follows:

Heavy combined feed, formed as hereinafter described, was subjected to thermal cracking

treatment in a heating coil and communicating reaction chamber at a temperature of 930° F. and under a superatmospheric pressure of approximately 250 pounds per square inch. The resulting conversion products were introduced to a vaporizer and separator operated at a superatmospheric pressure of 80 pounds per square inch wherein the vaporous conversion products were separated from the nonvaporous residue and the latter recovered as a product of the process. The vaporous conversion products were introduced to a fractionator operated at a superatmospheric pressure substantially the same as that employed in the vaporizer and separator and commingled with a 36° A. P. I. gravity-Mid-Continent crude oil. The mixture of conversion products and crude oil was subjected to fractionation to separate fractionated vapors having an end boiling point of 400° F. from the higher boiling hydrocarbons which were condensed and collected as light and heavy combined feeds and the heavy combined feed supplied to the heating coil, as previously described.

The fractionated vapors were commingled with the light combined feed and the mixture heated to a temperature of approximately 750° F. after which it was subjected to contact at a superatmospheric pressure of 60 pounds per square inch and at a liquid space velocity of 1 with a silica-alumina-zirconia catalyst in a low temperature cracking zone. The conversion products from the low temperature cracking zone were subjected to fractionation in the fractionator operated at a superatmospheric pressure of 40 pounds per square inch to separate fractionated vapors having an end boiling point of 300° F. from the higher boiling hydrocarbons. The latter were condensed as reflux condensate and supplied to the thermal cracking treatment. The 300 end point fractionated vapors were subjected to cooling and condensation and the resulting distillate and gas collected and separated and recovered as products of the process.

This operation yielded approximately 58% of 300 end point gasoline having a bromine number of 4 and an octane rating of 71 which was raised to approximately 92 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 low olefin content which comprises thermally cracking hydrocarbon oil heavier than gasoline to produce gasoline therefrom, introducing the resultant cracked gasoline-containing vapors to a fractionating zone maintained at a temperature above the boiling point of gasoline, additionally introducing to said zone a heavy hydrocarbon charging oil containing a sufficient amount of saturated hydrocarbons, vaporizable under the conditions prevailing in said zone, to saturate the major portion of the olefin content of the cracked gasoline in the manner hereinafter set forth, fractionating the cracked vapors and the charging oil in said zone and supplying resultant heavy reflux condensate and residual charging oil to the thermal cracking step as said oil heavier than gasoline, removing from the fractionating zone the cracked gasoline and a sufficient quantity of the saturated components of the charging oil to effect said olefin saturation and supplying the same in admixture to a catalytic conversion zone containing a cracking catalyst, subjecting the mixture to the action of said catalyst at a temperature of about 750° F. and a liquid space velocity of about one to saturate at least the major portion of the olefin content of the cracked gasoline, and fractionating and condensing the vaporous products of the catalytic treatment.

2. The process as defined in claim 1 further characterized in that reflux condensate formed by the last-mentioned fractionating step is supplied to the thermal cracking operation.

3. The process as defined in claim 1 further characterized in that said charging oil is a crude petroleum whose straight-run gasoline content is supplied to the catalytic conversion zone with the cracked gasoline to constitute a substantial part, at least, of said saturated components.

4. The process as defined in claim 1 further characterized in that the cracked gasoline is passed in vaporous form from the fractionating zone to the catalytic conversion zone.

5. The process as defined in claim 1 further characterized in that the cracked gasoline from the fractionating zone is condensed and separated from incondensable gases prior to its introduction to the catalytic conversion zone.

6. A process for producing motor fuel of high octane rating and low olefin content which comprises thermally cracking hydrocarbon oil heavier than gasoline to produce gasoline therefrom, introducing the resultant cracked gasoline-containing vapors to a fractionating zone maintained at a temperature above the boiling point of gasoline, additionally introducing to said zone a heavy hydrocarbon charging oil containing a sufficient amount of saturated hydrocarbons, vaporizable under the conditions prevailing in said zone, to saturate the major portion of the olefin content of the cracked gasoline in the manner hereinafter set forth, fractionating the cracked vapors and the charging oil in said zone and supplying resultant heavy reflux condensate and residual charging oil to the thermal cracking step as said oil heavier than gasoline, removing from the fractionating zone the cracked gasoline and a sufficient quantity of the saturated components of the charging oil to effect said olefin saturation and supplying the same in admixture to a catalytic conversion zone containing a cracking catalyst, subjecting the mixture to the action of said catalyst at a temperature in the approximate range of 500° to 800° F. for a contact time sufficient to saturate at least the major portion of the olefin content of the cracked gasoline, at least a portion of said saturated components supplied to the catalytic conversion zone being separated as an intermediate reflux condensate in the fractionating zone, and fractionating and condensing the vaporous products of the catalytic treatment.

ELMER R. KANHOFER.