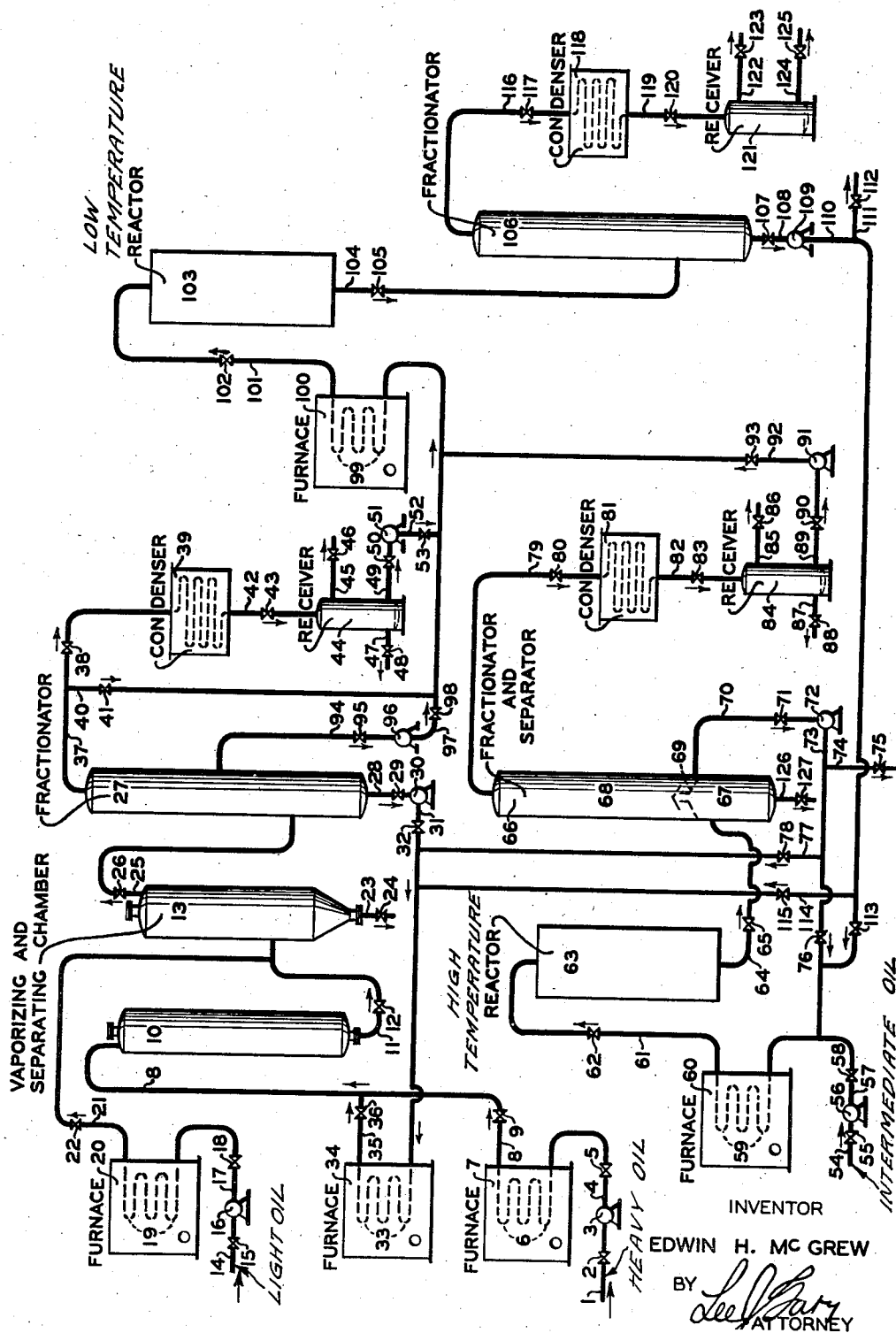


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## HYDROCARBON CONVERSION

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9 Claims. (Cl. 196—49)

This invention relates to a process for converting hydrocarbon oils into substantial yields of gasoline of high octane rating, relatively low olefin content, and low potential gum content. More specifically, it relates to a process involving a series of individual cooperative steps combined in a novel and advantageous manner so that each of several types of hydrocarbon oils treated are subjected to the optimum conditions for the production of motor gasoline.

The invention involves principally thermal cracking treatment of a relatively heavy hydrocarbon oil, such as, for example, reduced crude oil, with concurrent thermal cracking treatment of the recycle obtained therefrom, thermal reforming treatment of a relatively light hydrocarbon oil, such as, for example, gasoline, naphtha, or kerosene, common fractionation of the conversion products from the thermal cracking and reforming treatments, high temperature catalytic cracking treatment of an intermediate oil, such as gas-oil, and low temperature catalysis of the gasolines produced in the thermal cracking and reforming treatments, and high temperature catalytic cracking treatment in commingled state with light reflux condensate formed in the thermal cracking treatments to produce a gasoline of high octane rating and relatively low olefin content.

The term "thermal cracking treatment" as used throughout the present specification and claims refers to the conversion of heavy hydrocarbons into lighter hydrocarbons by heat and pressure, and in all instances involves the scission of carbon to carbon bonds. The term "thermal reforming treatment," on the other hand, refers to the treatment of relatively light hydrocarbons to improve their octane rating and may involve the scission of carbon to carbon bonds, the scission of carbon to hydrogen bonds, cyclization, and many other reactions of lesser importance. The term "high temperature catalytic cracking treatment" refers to the treatment of hydrocarbon oils in the presence of catalytically active materials at temperatures ranging, for example, from 800 to 1200° F. and at pressures varying from substantially atmospheric to 200 pounds or more per square inch to effect substantial conversion to gasoline boiling range hydrocarbons, and ordinarily involves the scission of carbon to carbon bonds, although other reactions such as cyclization and the scission of carbon to hydrogen bonds may also take place. The term "low temperature catalysis" refers to the treatment of hydrocarbons at relatively low temperatures

ranging, for example, from 500 to 900° F. and at pressures ranging from substantially atmospheric to 200 pounds or more per square inch in the presence of a catalyst of essentially the same composition as that employed in the high temperature catalytic cracking treatment, and the principal reactions involved are essentially hydrogen rearrangements.

The gasolines from thermal cracking, thermal reforming, and high temperature catalytic cracking usually contain a relatively high percentage of olefinic hydrocarbons which, although tending to improve the octane rating, are potential gum formers. The acid heat test of gasolines containing relatively high percentages of olefinic hydrocarbons, in addition, is generally high while the susceptibility to added antiknocking agents is relatively low, thereby rendering gasolines produced in such processes unfit for aviation purposes. Gasolines rich in paraffinic hydrocarbons, preferably containing high percentages of isomeric paraffinic hydrocarbons, and in some instances containing aromatic hydrocarbons, on the other hand, are particularly useful as an aviation fuel because of the relatively low acid heat test and good susceptibility to added antiknocking agents, such as tetraethyl lead.

It has been found that when the olefin-containing gasolines produced by non-catalytic and high temperature catalytic cracking methods are subjected to contact with a catalyst of essentially the same composition as that employed in the catalytic cracking treatment but at lower space velocities and lower temperatures with light recycle from a non-catalytic cracking treatment, a substantially saturated gasoline product is obtained. Whereas, in high temperature catalytic cracking treatments temperatures on the order of 800 to 1200° F. are employed with pressures of from substantially atmospheric to 200 pounds or more per square inch with space velocities of from 2 to 6 volumes of liquid hydrocarbon material per volume of catalyst per hour, in the low temperature treatment temperatures on the order of 500 to 900° F. are employed with pressures of from substantially atmospheric to 200 pounds or more per square inch and with space velocities of from .5 to 2.

The reactions involved in the low temperature treatment are essentially those of transferring hydrogen from the heavier hydrocarbons to the lighter olefinic hydrocarbons to form paraffinic hydrocarbons, although cracking, cyclization, and isomerization may also be involved. It is believed that in the low temperature catalysis sat-

urated hydrocarbons and particularly the naphthenic hydrocarbons of the recycle oil act as hydrogen donors to the olefinic hydrocarbons of the gasoline, while the olefinic hydrocarbons become saturated to form aliphatic 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 two or three molecules of hydrogen which attach to the unsaturated olefinic hydrocarbons may also take place. However, since the invention is concerned primarily with a process in which the various reactions may be conducted, further discussion with regard to the chemical reactions which may possibly be involved is unnecessary for a full understanding of the invention, which is to be described in more detail later.

In one specific embodiment the invention comprises subjecting a relatively heavy hydrocarbon oil to thermal cracking treatment in a heating coil, concurrently subjecting reflux condensate, formed as hereinafter described, to thermal cracking treatment in a separate heating coil, commingling the hot conversion products from the last mentioned heating coil with those from the first mentioned heating coil and supplying the mixture to a communicating reaction chamber to effect substantial further conversion thereof, subjecting a relatively light hydrocarbon oil to thermal reforming treatment in a heating coil, commingling the conversion products from said thermal reforming treatment and the conversion products from said reaction chamber and supplying the commingled material to a vaporizing and separating chamber to separate a non-vaporous liquid residue from the vaporous conversion products, recovering the former, supplying said vaporous conversion products to a fractionator to separate by fractionation the gasoline boiling range materials from the higher boiling components, condensing the latter as light and heavy reflux condensate, supplying said heavy reflux condensate to the second mentioned heating coil, for treatment as aforesaid, simultaneously with the thermal cracking and thermal reforming treatments, heating and vaporizing a mixture comprising essentially an oil boiling intermediate to the two first mentioned charging oils and reflux condensates formed in the subsequent high and low temperature catalytic treatments, subjecting the heated vapors to contact with a catalyst mass in a high temperature catalytic cracking zone, fractionating the vaporous conversion products from said high temperature catalytic cracking zone to separate gasoline boiling range materials from the higher boiling components, condensing the latter as reflux condensate and subjecting it to high temperature catalytic treatment as aforesaid, commingling the gasoline boiling range materials from the thermal cracking and reforming treatments and the high temperature catalytic cracking treatment with said light reflux condensate, heating the mixture and supplying the heated mixture to contact with a catalyst in a low temperature catalytic zone, fractionating the conversion products from said low temperature catalytic zone to separate fractionated vapors of the desired end boiling point from the higher boiling hydrocarbons, recovering said fractionated vapors as a product of the process, condensing said higher boiling hydrocarbons as reflux condensate and

subjecting the latter to high temperature catalytic treatment as aforesaid.

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 the use of the specific form of apparatus herein shown and that various forms of apparatus herein described may be used without departing from the broad scope of the invention.

Referring now to the drawing, a relatively heavy hydrocarbon oil, such as, for example, a topped or reduced crude oil, is introduced through line 1 and valve 2 to pump 3, which discharges through line 4 and valve 5 into heating coil 6. The oil in passing through heating coil 6 is raised to the desired cracking temperature, which may range, for example, from 800 to 950° F. and is maintained at this temperature for a sufficient period of time so that substantial cracking may be effected, the heat necessary to raise the oil to the desired temperature and to furnish the heat of cracking being supplied by furnace 7. The hot conversion products leave heating coil 6 through line 8 at a super-atmospheric pressure ranging, for example, from 200 to 600 pounds or more per square inch and are directed through valve 9, commingled with other hot conversion products formed by cracking heavy reflux condensate, as hereinafter described, and the mixture thereafter introduced to reaction chamber 10 wherein it is subjected to prolonged conversion at the cracking temperature. Reaction chamber 10 is preferably operated at a super-atmospheric pressure substantially the same as that employed on the outlet of heating coil 6 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 10 are directed through line 11 and valve 12 into vaporizing and separating chamber 13 for treatment, as hereinafter described. Simultaneously with the thermal treatments being accomplished in heating coils 6 and 33, a relatively light hydrocarbon oil, such as, for example, gasoline, naphtha, or kerosene, or any mixture thereof, is introduced through line 14 and valve 15 to pump 16, which discharges through line 17 and valve 18 into heating coil 19. The oil in passing through heating coil 19 is subjected to thermal reforming treatment at a temperature ranging, for example, from 950 to 1050° F. by means of heat supplied from furnace 20. The conversion products leaving heating coil 19 at a pressure ranging, for example, from 500 to 1200 pounds or more per square inch are directed through line 21 and valve 22 to line 11 where they commingle with the vaporous and liquid conversion products from reaction chamber 10.

Vaporizing and separating chamber 13 is preferably operated at a reduced pressure relative to that employed in reaction chamber 10 and may range, for example, from 50 to 250 pounds or more per square inch. The liquid conversion products are subjected to substantial further vaporization to form a non-vaporous liquid residue, the latter being withdrawn from chamber 13 by way of line 23 and valve 24 and directed to cooling and storage or to further treatment as desired.

The vaporous conversion products separated in chamber 13, together with the vapors evolved

therein, are directed through line 25 and valve 26 into fractionator 27 which is preferably maintained at a superatmospheric pressure of the same order as that employed in chamber 13. The vaporous conversion products introduced to fractionator 27 are subjected to fractionation therein to form light and heavy reflux condensate and to separate fractionated vapors which may comprise gasoline boiling range hydrocarbons or may, when desired, include hydrocarbons boiling above the range of gasoline. The heavy reflux condensate is directed through line 28 and valve 29 to pump 30, which discharges through line 31 and valve 32 into heating coil 33. The heavy reflux condensate in passing through heating coil 33 is raised to the desired cracking temperature which may range, for example, from 900 to 1030° F. and is maintained at the cracking temperature for a sufficient period of time to effect substantial conversion thereof. The conversion products leave heating coil 33 at a substantial superatmospheric pressure which may range from 400 to 300 pounds or more per square inch and are directed through line 35 and valve 36 into line 3 for treatment as previously described.

Fractionated vapors separated in fractionator 27 are directed from the upper portion thereof through line 37 and a portion corresponding to the amount required for cooling and refluxing fractionator 27 is directed through valve 38 to cooling and condensation in condenser 39, the residual portion being directed through line 40 and valve 41 into line 97, for treatment as hereinafter described. If, on the other hand, it is desirable to subject all of the fractionated vapors to cooling and condensation, valve 41 in line 40 may be closed and all of said fractionated vapors directed through valve 38 to cooling and condensation in condenser 39. In any case, the distillate from condenser 39, together with undissolved and uncondensed gases, is directed through line 42 and valve 43 to receiver 44, wherein the normally liquid hydrocarbons are separated from the undissolved and uncondensed gaseous hydrocarbons, the latter being withdrawn from receiver 44 by way of line 45 and valve 46. When the distillate collected in receiver 44 is to be used solely for cooling and refluxing in fractionator 27, all of it may be withdrawn therefrom, by well known means not shown, and introduced into the upper portion of fractionator 27. On the other hand, it may be desirable at times to recover a portion or all of the distillate not required for refluxing in fractionator 27, and this may be accomplished by withdrawing the distillate through line 47 and valve 48. The preferred method, however, and one more in accord with the object of the invention, is to direct the distillate not employed as a refluxing and cooling medium through line 49 and valve 50 to pump 51, which discharges through line 52 and valve 53 into line 97, for treatment as hereinafter described.

Concurrently with the thermal cracking and reforming treatments an intermediate oil, such as, for example, kerosene or gas-oil, is introduced through line 54 and valve 55 into pump 56, which discharges through line 57 and valve 58 and the oil commingled, when desired, with reflux condensate formed as hereinafter described. In any case, the hydrocarbon oil in line 57 is directed into heating coil 59 wherein it is substantially completely vaporized and raised to the desired temperature which may range, for example, from 800 to 1200° F. without substantial pyrolytic

cracking thereof, the heat being supplied from furnace 60. The heated vapors leaving heating coil 59 at a pressure ranging, for example, from substantially atmospheric to 200 pounds or more per square inch are directed through line 61 and valve 62 into reactor 63 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 by means of heat supplied from an external source.

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 63 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 ac-

complished 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 63 are directed through line 64 and valve 65 into separating zone 67 which forms the lower portion of fractionator and separator 66. Fractionator and separator 66 is preferably operated at a superatmospheric pressure substantially the same as that employed on the outlet of reactor 63. Non-vaporous liquid residue separated from the vaporous conversion products in zone 67 is withdrawn from the lower portion thereof by way of line 126 and valve 127, cooled and recovered or subjected to any desired further treatment. Vaporous conversion products separated in zone 67 are directed through separating tray 69 into fractionating zone 68 wherein they are subjected to fractionation to form reflux condensate and to separate fractionated vapors of the desired end boiling point. Fractionated vapors separated in zone 68 may comprise, for example, hydrocarbons boiling in the range of gasoline or, when desired, may include hydrocarbons boiling above the range of gasoline.

Reflux condensate formed within fractionating zone 68 is directed from the lower portion thereof through line 70 and valve 71 into pump 72. Pump 72 discharges through line 73 and a portion or all of the oil may be directed through line 74 and valve 75 and recovered as a product of the process. However, since reflux condensate produced in this manner is more valuable as a potential source of gasoline, the preferred method is to subject it to further cracking treatment either by catalytic or non-catalytic methods. When the reflux condensate in line 73 contains relatively high percentages of aliphatic hydrocarbons as compared to the concentration of aromatic hydrocarbons, the desired treatment would be to crack it in the presence of a catalyst, in which case the reflux condensate in line 73 would be directed through valve 76 into line 57, commingled therein with the intermediate oil and thereafter subjected to treatment as previously described. If, on the other hand, the reflux condensate contains relatively high percentages of aromatic hydrocarbons, the more desirable treatment would be cracking by non-catalytic means, in which case the oil in line 73 would be directed through line 77 and valve 78 into line 31, commingling therein with heavy reflux condensate, formed as previously described, and the mixture subjected to thermal cracking treatment in heating coil 33.

Although the above described procedures are the two preferred ones, it may be desirable, depending upon the type of operation employed, to introduce portions of the reflux condensate in line 73 to both high temperature catalytic cracking treatment and the thermal cracking treatment simultaneously.

Fractionated vapors separated in fractionating zone 68 are directed from the upper portion thereof through line 79 and valve 80 for cooling

and condensation in condenser 81. Distillate, together with undissolved and uncondensed gases in condenser 81, is directed through line 82 and valve 83 into receiver 84 wherein the distillate and undissolved and uncondensed normally gaseous hydrocarbons are collected and separated. Normally gaseous hydrocarbons separated in receiver 84 are directed from the upper portion thereof through line 85 and valve 86 and collected or subjected to any desired further treatment. A portion of the distillate collected and separated in receiver 84 is returned to the upper portion of fractionating zone 68, by well known means not shown, as a refluxing and cooling medium therein. When desired, the balance of the distillate collected and separated in receiver 84 may be recovered as a product of the process by withdrawing the same through line 87 and valve 88. The balance of the distillate collected in receiver 84, however, preferably and in accordance with the object of the invention, is subjected to further catalytic treatment in order to produce the gasoline which is substantially free of olefinic hydrocarbons. The balance of the distillate collected in receiver 84 may therefore be directed through line 89 and valve 90 to pump 91, which discharges through line 92 and valve 93 into line 97 for treatment as hereinafter described.

Light reflux condensate from fractionator 27 is directed through line 94 and valve 95 to pump 96, which discharges through line 97 and valve 98, the light reflux condensate commingling therein with the distillate separated in fractionator 27 and fractionator and separator 66, the mixture thereafter being supplied to heating coil 99. In some instances, depending upon the volume of saturated gasoline which may be used economically, it may be desirable to subject only one or portions of the separately formed distillates, in which case the other distillate or portions may be recovered as products of the process.

The oil introduced to heating coil 99 is raised to a temperature in the range of 500 to 900° F. without substantial pyrolytic cracking thereof by means of heat supplied from furnace 100. The heated oil leaving heating coil 99 at a pressure ranging, for example, from substantially atmospheric to 200 pounds or more per square inch is directed through line 101 and valve 102 into reactor 103 where it is subjected to contact with a cracking catalyst while maintaining the oil at substantially the same temperature as that employed on the outlet of heating coil 99. The catalyst employed in reactor 103 may be of the same composition as that employed and described in connection with reactor 63. The low and high temperature catalytic reactions differ essentially with respect to temperature and contact times employed, the reaction in reactor 63 being carried out at a relatively high temperature and short contact time, whereas the reaction in reactor 103 is carried out at a lower temperature and at a longer contact time. Reactors 63 and 103 may be essentially of 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 103 are directed through line 104 and valve 105 into fractionator 106 and maintained at substantially the same or at a reduced pressure relative to that employed on the outlet of reactor 103. The conversion products introduced to fractionator 106 are subjected to fractionation therein to form reflux condensate and to separate the gaso-

line boiling range hydrocarbons. Reflux condensate formed in fractionator 106 is directed through line 107 and valve 108 to pump 109. Pump 109 discharges through line 110 and a portion or all of the reflux condensate may be recovered as a product of the process by withdrawing the same through line 111 and valve 112. Reflux condensate formed in fractionator 106, however, is more advantageously utilized by subjecting it to further cracking treatment and preferably to the high temperature catalytic cracking treatment because of its relatively high hydrogen content as compared to the reflux condensate formed in the high temperature catalytic cracking treatment. This may be accomplished by directing the reflux condensate in line 110 through valve 113 into line 73 commingling with the reflux condensate formed in fractionating zone 58, the mixture thereafter being introduced to line 57 for treatment as previously described. In some instances, however, it may be desirable to subject a portion or all of the reflux condensate from fractionator 106 to thermal cracking treatment, in which case it may be directed through line 114 and valve 115 into line 31, commingling therein with the heavy reflux condensate from fractionator 27, the mixture thereafter being supplied to heating coil 33 for treatment as previously described.

Fractionated vapors from fractionator 106 are directed through line 116 and valve 117 to cooling and condensation in condenser 118. Distillate, together with undissolved and uncondensed gases from condenser 118, is directed through line 119 and valve 120 to collection and separation in receiver 121. Normally gaseous hydrocarbons collected and separated in receiver 121 are directed from the upper portion thereof through line 122 and valve 123 to storage or to any desired further treatment. A portion of the distillate collected in the lower portion of receiver 121 may be returned to the upper portion of fractionator 106, by well known means not shown, as a refluxing and cooling medium therein. The balance of the distillate collected in receiver 121 is removed therefrom by way of line 124 and valve 125 and recovered as a product of the process.

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

A 25° A. P. I. gravity Mid-Continent reduced crude oil was subjected to thermal cracking treatment in a heating coil at a temperature of 890° F. and at a superatmospheric pressure of 300 pounds per square inch. Concurrently, heavy reflux condensate, formed as hereinafter set forth, was subjected to thermal cracking treatment in a separate heating coil at a temperature of 940° F. and at a superatmospheric pressure of 500 pounds per square inch. The hot conversion products from both heating coils were commingled and the mixture introduced to a reaction chamber maintained at a superatmospheric pressure of approximately 275 pounds per square inch where it was subjected to prolonged conversion at the elevated temperature.

Substantially simultaneously, a 45° A. P. I. gravity hydrocarbon oil fraction, comprising straight-run gasoline, naphtha, and kerosene, was subjected to thermal reforming treatment in a heating coil at a temperature of 1010° F. and at a superatmospheric pressure of 750 pounds per

square inch. The conversion products from the reaction chamber and the last mentioned heating coil were commingled and the mixture introduced to a vaporizing and separating chamber maintained at a superatmospheric pressure of 75 pounds per square inch wherein vaporous conversion products and vapors formed due to the reduction in pressure were separated from the non-vaporous liquid residue and the latter recovered as a product of the process. The vapors introduced and evolved in the vaporizing and separating chamber were introduced to a fractionator operated under a superatmospheric pressure substantially the same as that maintained in the vaporizing and separating chamber to separate by fractionation high boiling components from the vapors boiling below 400° F. and to form light and heavy reflux condensate from said higher boiling components, the heavy reflux condensate being subjected to thermal cracking treatment, as previously described. Fractionated vapors were cooled and condensed and the resulting distillate and gas collected and separated.

In another step of the process a 35° A. P. I. gravity straight-run gas-oil fraction was vaporized and heated to a temperature of 950° F. with little or no pyrolytic cracking, and the vapors were subjected to contact with a silica-alumina-zirconia catalyst at a superatmospheric pressure of approximately 60 pounds per square inch while maintaining the vapors at substantially the same temperature as that employed on the outlet of the heating coil. The conversion products in this case were introduced to a separating zone operated at a superatmospheric pressure substantially the same as that employed on the outlet of the catalytic conversion zone to separate a non-vaporous liquid residue from the vaporous conversion products, the former recovered as a product of the process, and the vaporous conversion products subjected to fractionation to form reflux condensate and to separate as vapors hydrocarbons boiling below 400° F. The reflux condensate was returned to the heating coil for further conversion while the fractionated vapors were subjected to cooling and condensation and the resulting distillate and gas collected and separated.

The distillate separated in the thermal and catalytic cracking steps were commingled with the light reflux condensate formed in the first mentioned fractionator, the mixture heated to a temperature of approximately 750° F. and thereafter subjected to contact with a cracking catalyst in a low temperature conversion zone at a pressure of approximately 100 pounds per square inch. The conversion products from the low temperature conversion zone were introduced to a fractionator operated at a superatmospheric pressure substantially the same as that employed on the outlet of the conversion zone wherein the heavier components were separated by fractionation from the vapors boiling below 300° F. and the former condensed as reflux condensate in the fractionating zone. The reflux condensate from this zone was supplied to the heating coil of the high temperature catalytic cracking treatment while the fractionated vapors were subjected to cooling and condensation and recovered as distillate and gas.

The above described operation based on a total feed distributed approximately as follows: 40% reduced crude, 30% gasoline, naphtha, and kerosene, and 30% gas-oil resulted in a yield of ap-

proximately 69% of 300° F. end point gasoline having an octane rating of 78 and a bromine number of 7. With the addition of 6 cc. of tetraethyl lead the octane rating was raised to 91. In addition, approximately 14% of non-vaporous liquid residue was obtained with an A. P. I. gravity of 10, the balance being attributed principally to gas and loss.

I claim as my invention:

1. A process for the conversion of hydrocarbon oils to produce gasoline containing a relatively small amount of olefinic hydrocarbons, which comprises subjecting a relatively high boiling hydrocarbon oil to thermal cracking treatment, concurrently therewith subjecting a relatively low boiling hydrocarbon oil to thermal reforming treatment, commingling the conversion products and fractionating to form light and heavy reflux condensate and to separate vapors boiling in the range of gasoline, simultaneously in another step of the process subjecting an oil boiling intermediate to the two first mentioned oils to high temperature catalytic cracking treatment, commingling the gasoline from said thermal cracking, thermal reforming, and high temperature catalytic cracking treatments with the light reflux condensate from said thermal cracking treatment, and subjecting the mixture to the action of a cracking catalyst at a temperature of about 500-900° F. for a sufficient time to effect substantial saturation of the olefin content of the gasoline, said process being further characterized in that vapors boiling in the range of gasoline from the thermal cracking treatment are commingled with the distillate from the high temperature catalytic cracking treatment and the light reflux condensate from the thermal cracking treatment without prior cooling and condensation thereof.

2. A process for the conversion of hydrocarbon oils to produce gasoline containing a relatively small amount of olefinic hydrocarbons, which comprises subjecting a relatively high boiling hydrocarbon oil to thermal cracking treatment in a heating coil, concurrently therewith subjecting heavy reflux condensate, formed as hereinafter described, to thermal cracking treatment in a second heating coil, commingling the conversion products from both heating coils and subjecting the mixture to prolonged conversion in a reaction chamber, subjecting a relatively low boiling hydrocarbon oil to thermal reforming treatment in a third heating coil, commingling the conversion products from said thermal reforming treatment and said reaction chamber and fractionating the vaporous fraction therefrom to form light and heavy reflux condensate and to separate vapors boiling in the range of gasoline, supplying the heavy reflux condensate to said second heating coil, as previously described, in another step of the process subjecting an oil boiling intermediate to the two first mentioned oils to high temperature catalytic cracking treatment, fractionating the vaporous conversion products from said high temperature catalytic cracking treatment to form reflux condensate and to separate fractionated vapors boiling in the range of gasoline, commingling the gasolines from the thermal cracking, thermal reforming, and high temperature catalytic cracking treatments with the light reflux condensate from said thermal cracking treatment, and subjecting the mixture to low temperature catalysis.

3. A process for the conversion of hydrocarbon oils to produce gasoline containing a relatively small amount of olefinic hydrocarbons, which

comprises subjecting a relatively high boiling hydrocarbon oil to thermal cracking treatment in a heating coil, concurrently therewith subjecting heavy reflux condensate, formed as hereinafter described, to thermal cracking treatment in a second heating coil, commingling the conversion products from both heating coils and subjecting the mixture to prolonged conversion in a reaction chamber, subjecting a relatively low boiling hydrocarbon oil to thermal reforming treatment in a third heating coil, commingling the conversion products from said thermal reforming treatment and said reaction chamber, separating vaporous conversion products from the non-vaporous liquid residue and recovering the latter, fractionating said vaporous conversion products to form light and heavy reflux condensate and to separate vapors boiling in the range of gasoline, supplying the heavy reflux condensate to said second heating coil, as previously described, cooling and condensing said vapors and recovering the resulting distillate and gas, heating and vaporizing an oil boiling intermediate to the two first mentioned oils in a fourth heating coil and subjecting the resulting vapors to high temperature catalytic cracking treatment, separating vaporous conversion products from the non-vaporous liquid residue formed in said high temperature catalytic cracking treatment, recovering the latter, fractionating said vaporous conversion products from said high temperature catalytic cracking treatment to form reflux condensate and to separate fractionated vapors boiling in the range of gasoline, cooling and condensing said fractionated vapors and recovering the resulting distillate and gas, commingling the distillates from the thermal cracking, thermal reforming, and high temperature catalytic cracking treatments with the light reflux condensate from the thermal cracking treatments, heating the mixture and subjecting the heated mixture to low temperature catalysis, fractionating the conversion products from said low temperature catalysis to separate gasoline boiling range hydrocarbons which are cooled and collected as a product of the process.

4. A process such as defined in claim 3 wherein the reflux condensate from the high temperature catalytic cracking treatment is subjected to further treatment in the same step.

5. A process such as defined in claim 3 wherein the reflux condensate from the high temperature catalytic cracking treatment is supplied to the thermal cracking treatment in commingled state with the heavy reflux condensate.

6. A process such as defined in claim 3 wherein products of the low temperature catalysis, heavier than gasoline, are supplied to the high temperature catalytic cracking treatment.

7. A process such as defined in claim 3 wherein products of the lower temperature catalysis, heavier than gasoline, are supplied to the thermal cracking treatment in commingled state with the heavy reflux condensate.

8. A process for the conversion of hydrocarbon oils to produce gasoline containing a relatively small amount of olefinic hydrocarbons, which comprises subjecting a relatively high boiling hydrocarbon oil to thermal cracking treatment in a heating coil, concurrently therewith subjecting heavy reflux condensate, formed as hereinafter described, to thermal cracking treatment in a second heating coil, commingling the conversion products from both heating coils and subjecting the mixture to prolonged conversion in a reac-

tion chamber, subjecting a relatively low boiling hydrocarbon oil to thermal reforming treatment in a third heating coil, commingling the conversion products from said thermal reforming treatment and said reaction chamber, separating vaporous conversion products from the non-vaporous liquid residue and recovering the latter, fractionating said vaporous conversion products to form light and heavy reflux condensate and to separate vapors boiling in the range of gasoline, supplying the heavy reflux condensate to said second heating coil, as previously described, cooling and condensing said vapors and recovering the resulting distillate and gas, heating and vaporizing an oil boiling intermediate to the two first mentioned oils in a fourth heating coil and subjecting the resulting vapors to high temperature catalytic cracking treatment in the presence of silica composited with a compound selected from the group consisting of alumina and zirconia while maintaining the vapors at a cracking temperature, separating vaporous conversion products from the non-vaporous liquid residue formed in said high temperature catalytic cracking treatment, recovering the latter, fractionating said vaporous conversion products from said high temperature catalytic cracking treatment to form reflux condensate and to separate fractionated vapors boiling in the range of gasoline, cooling and condensing said fractionated vapors and recovering the resulting distillate and gas, commingling the distillates from the thermal cracking, thermal reforming, and high temperature catalytic cracking treatments with the light reflux condensate from the thermal cracking treatments, heating the mixture and subjecting the heated mixture to low temperature catalysis in the presence of a cracking catalyst of essentially the same composition as that hereinbefore set forth while maintaining the temperature of the mixture substantially constant, fractionating the conversion products from said low temperature catalysis to separate gasoline boiling range hydrocarbons which are cooled and collected as a product of the process.

9. A process for the conversion of hydrocarbon oils to produce gasoline containing a relatively small amount of olefinic hydrocarbons, which comprises subjecting a relatively high boiling hydrocarbon oil to a thermal cracking treatment in a heating coil at a temperature of from 800 to 950° F. and at a superatmospheric pressure of from 200 to 600 pounds per square inch, concurrently therewith subjecting heavy reflux condensate, formed as hereinafter described, to thermal cracking treatment in a second heating

coil at a temperature of from 900 to 1030° F. and at a superatmospheric pressure of from 400 to 800 pounds per square inch, commingling the conversion products from both heating coils and subjecting the mixture to prolonged conversion in a reaction chamber, subjecting a relatively low boiling hydrocarbon oil to thermal reforming treatment in a third heating coil at a temperature of from 950 to 1050° F. and at a superatmospheric pressure of from 500 to 1200 pounds per square inch, commingling the conversion products from said thermal reforming treatment and said reaction chamber, separating vaporous conversion products from the non-vaporous liquid residue and recovering the latter, fractionating said vaporous conversion products to form light and heavy reflux condensate and to separate vapors boiling in the range of gasoline, supplying the heavy reflux condensate to said second heating coil, as previously described, cooling and condensing said vapors and recovering the resulting distillate and gas, heating and vaporizing an oil boiling intermediate to the two first mentioned oils in a fourth heating coil and subjecting the resulting vapors to high temperature catalytic cracking treatment in the presence of silica composited with a compound selected from the group consisting of alumina and zirconia at a temperature of from 800 to 1200° F. and at a pressure of from substantially atmospheric to 200 pounds per square inch, separating vaporous conversion products from the non-vaporous liquid residue formed in said high temperature catalytic cracking treatment, recovering the latter, fractionating said vaporous conversion products from said high temperature catalytic cracking treatment to form reflux condensate and to separate fractionated vapors boiling in the range of gasoline, cooling and condensing said fractionated vapors and recovering the resulting distillate and gas, commingling the distillates from the thermal cracking, thermal reforming, and high temperature catalytic cracking treatments with the light reflux condensate from the thermal cracking treatments, heating the mixture and subjecting the heated mixture to low temperature catalysis in the presence of a cracking catalyst of essentially the same composition as hereinbefore set forth at a temperature of from 500 to 900° F. and at a pressure of from substantially atmospheric to 200 pounds per square inch, fractionating the conversion products from said low temperature catalysis to separate gasoline boiling range hydrocarbons which are cooled and collected as a product of the process.

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