

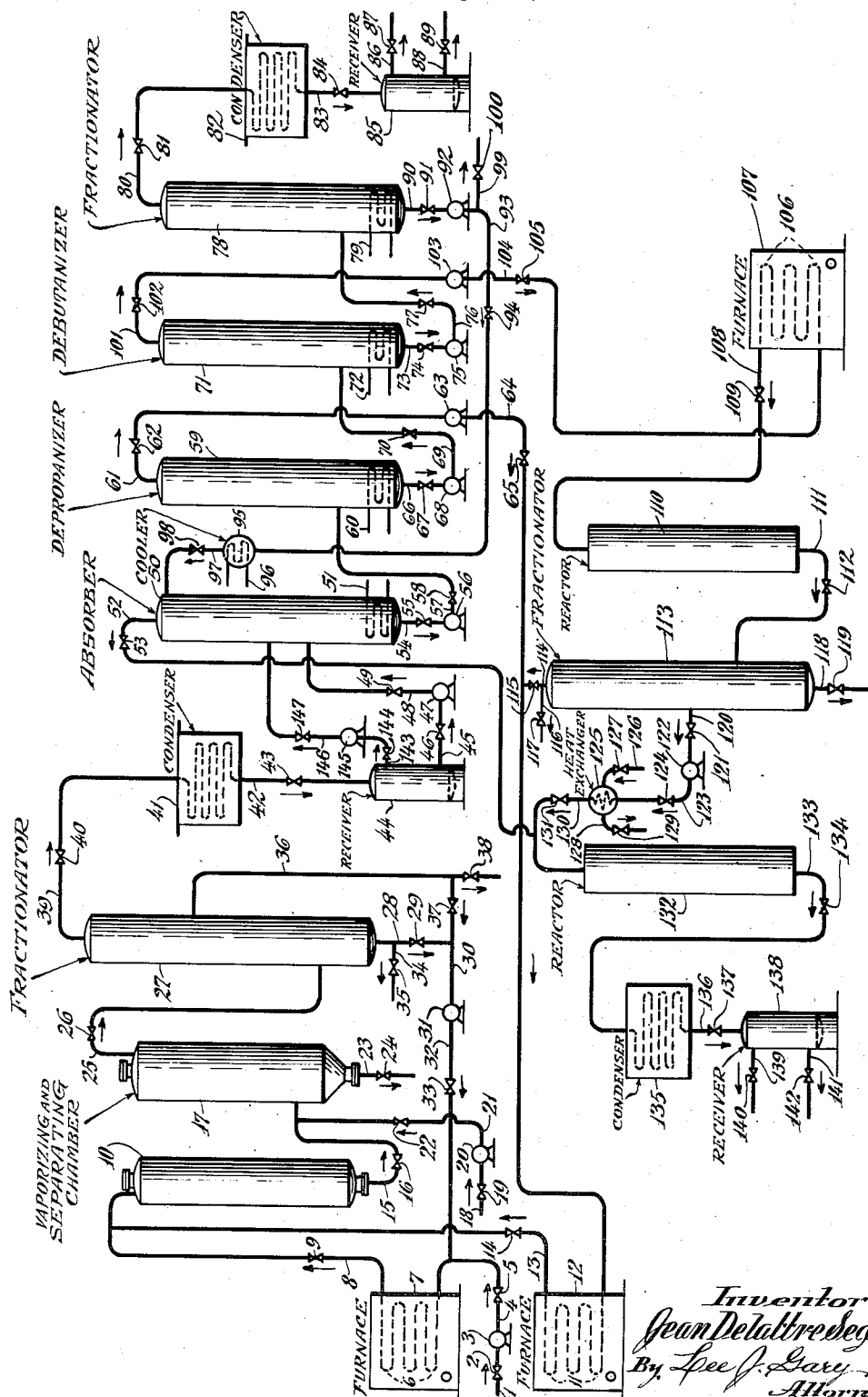
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HYDROCARBON CONVERSION

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HYDROCARBON CONVERSION

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This invention relates to a process for producing both motor and aviation gasolines. More specifically, it is concerned with a process which involves a series of interdependent steps combined in a novel and advantageous manner so that the hydrocarbons are treated under optimum conditions for their conversion into more valuable products.

The invention broadly covers thermal cracking of hydrocarbon oils in substantially the vapor phase to produce motor gasoline, pyrolytic treatment of C₂ and C₃ gaseous hydrocarbons, together with essentially only C₄ paraffinic hydrocarbons, all of which are formed in the process, to produce pyrolytic polymer gasoline, selective polymerization treatment of the C₄ fraction formed in the process, and hydrogenation of the iso-octenes from said selective polymerization treatment with the hydrogen contained in the light gas fraction formed in the process to produce iso-octane.

In the vapor phase cracking of normally liquid hydrocarbons relatively large quantities of normally gaseous hydrocarbons are produced, a high percentage of which are C₄ hydrocarbons and particularly the olefinic hydrocarbons of the C₄ fraction. The C₄ olefinic hydrocarbons may be polymerized in the presence of suitable catalysts and under selected conditions to yield iso-octenes. The iso-octenes upon hydrogenation are converted to iso-octane which is valuable as an aviation gasoline because of its relatively high octane rating and low acid heat test.

In the pyrolytic treatment of the C₂ and C₃ hydrocarbons, together with the residual C₄ hydrocarbons from the catalytic polymerization treatment, a pyrolytic polymer is obtained which is valuable as a blending agent for ordinary motor fuel and, in addition, in this treatment unsaturated C₄ hydrocarbons are produced, probably due at least in part to polymerization of the lighter normally gaseous hydrocarbons and to dehydrogenation of the C₄ paraffinic hydrocarbons subjected to treatment therein. The unsaturated C₄ hydrocarbons formed in the pyrolytic gas treatment after separation from the lighter gases and from the normally liquid hydrocarbons may be supplied to the polymerization treatment for conversion into iso-octenes.

One specific embodiment of the invention comprises subjecting combined feed comprising a relatively light hydrocarbon oil boiling above the range of gasoline and reflux condensate, formed as hereinafter described, to thermal cracking treatment in a heating coil and communicating

reaction chamber in substantially the vapor phase, concurrently therewith subjecting normally gaseous hydrocarbons formed in the process to pyrolytic treatment in a separate heating coil and thereafter supplying the conversion products from said separate heating coil to said reaction chamber, cooling the conversion products from said reaction chamber by commingling therewith a relatively heavy hydrocarbon oil introduced from an outside source, separating the mixture of conversion products and cooling oil into a non-vaporous liquid residue and vapors which include the vaporous conversion products, fractionating said vapors to form reflux condensate and to separate fractionated vapors boiling in the range of gasoline, supplying at least a portion of said reflux condensate to said thermal cracking treatment, as aforesaid, cooling and condensing said fractionated vapors and recovering the resulting distillate and gas, separating said distillate and said gas into a methane-hydrogen fraction, a C₂ and C₃ fraction, a C₄ fraction, and a gasoline fraction, recovering said gasoline fraction, commingling said C₂ and C₃ fraction with the residual C₄ fraction, separated as hereinafter set forth, and subjecting the mixture to the pyrolytic gas treatment, as previously set forth, subjecting said C₄ fraction to selective polymerization treatment to convert the olefins to iso-octenes, fractionating the conversion products from said selective polymerization treatment to separate a heavy polymer fraction, an iso-octene fraction, and a residual C₄ fraction, commingling said residual C₄ fraction with said C₂ and C₃ fraction, as previously described, recovering said heavy polymer fraction, subjecting said iso-octene fraction to hydrogenation treatment in commingled state with said methane-hydrogen fraction, and recovering the resulting iso-octane as a product of the process.

In the operation of the process, normally liquid hydrocarbons comprising a relatively light hydrocarbon oil, such as gas-oil and reflux condensate formed in the process, 90% of which preferably boils below 700° F., are subjected to cracking treatment in substantially the vapor phase to form conversion products which contain both gasoline boiling range hydrocarbons and normally gaseous hydrocarbons in addition to the heavy hydrocarbon components. The conversion products are separated into gas, gasoline, intermediate conversion products, and residue, and the latter recovered as a product of the process. Ordinarily, all of the intermediate conversion products, consisting of hydrocarbons boil-

ing above gasoline, are returned to the cracking step, however, when heavy components are present, it is preferred that selected portions only, such as those which have 90% boiling below 700° F. in an Engler distillation, be returned to the cracking system. The gases are preferably separated into selected fractions, such as a methane-hydrogen fraction, a C₂-C₃ fraction, and a C₄ fraction. The C₄ fraction is subjected to a catalytic polymerization treatment to convert the olefins contained therein under selected conditions of temperature and pressure into iso-octenes, which upon hydrogenation with hydrogen obtained from the methane-hydrogen fraction are converted to iso-octane. The C₂-C₃ fraction, together with the residual C₄ fraction from the polymerization treatment, is subjected to pyrolytic treatment to form pyrolytic polymer gasoline and more C₄ olefinic gases.

Heavy oils, such as, for example, topped or reduced crude, which under vapor phase conditions have a strong tendency to form coke, may be utilized in the process, when desired, as a cooling oil and the lighter components thereof subjected to cracking treatment. This may be accomplished by commingling the heavy oil with the conversion products from the vapor phase cracking system and the pyrolytic gas treatment and thereafter separating and removing the non-vaporous portion in commingled state with the non-vaporous liquid residue formed in the cracking treatment and separating the vaporous portion thereof in commingled state with the vaporous conversion products.

The accompanying diagrammatic drawing illustrates in conventional side elevation one specific form of the apparatus in which the process of the invention may be conducted. It is not drawn to any exact or relative scale and furthermore it is not intended that the invention should be limited to the specific form of apparatus herein disclosed. I may, for example, employ other means for separating the hydrocarbon gases, all of which are included within the broad scope of the invention. The invention is limited only with respect to the material described and that disclosed in the prior art.

Referring now to the drawing, a hydrocarbon oil suitable for cracking in the vapor phase, such as, for example, a wide boiling range mixture of relatively low boiling range hydrocarbons, or any fraction thereof, such as gas-oil, is introduced through line 1 and valve 2 to pump 3, which discharges through line 4 and valve 5. The hydrocarbon oil in line 4 is commingled with reflux condensate, formed as hereinafter described, and the mixture introduced to heating coil 6. The mixture introduced to heating coil 6 is substantially completely vaporized therein and raised to the desired cracking temperature which may range, for example, from 975 to 1150° F. The heated vapors are maintained at a cracking temperature for a sufficient period of time to effect substantial conversion thereof, the heat of vaporization and cracking being supplied by furnace 7. The conversion products leaving heating coil 6 at a pressure ranging, for example, from 5 to 150 pounds or more per square inch are directed through line 8 and valve 9 into reaction chamber 10 where they are subjected to substantial further conversion by means of their contained heat. Reaction chamber 10 is operated at substantially the same or at a reduced pressure relative to that employed on the outlet of the heating coil and is also preferably insulated

to reduce radiation losses therefrom, although no insulation is shown in this drawing.

In another step of the process, concurrently with the vapor phase cracking treatment in heating coil 6 and reaction chamber 10, normally gaseous hydrocarbons, separated as hereinafter described, are introduced to heating coil 11 where they are subjected to pyrolytic treatment at temperatures ranging, for example, from 900 to 1400° F. and under a superatmospheric pressure of from 500 to 3000 pounds or more per square inch. The conversion products from heating coil 11 are directed through line 13 and valve 14 into line 8 where they commingle with the conversion products from heating coil 6 prior to their introduction into reaction chamber 10. The conversion products from reaction chamber 10 are directed through line 15 and a valve 16, preferably cooled to arrest the cracking reaction by commingling therewith a hydrocarbon oil, and the mixture thereafter introduced to a vaporizing and separating chamber 17.

The cooling oil, which may comprise, for example, topped or reduced crude or any fraction thereof, or, when desired lighter hydrocarbon oils, is introduced through line 18 and valve 19 to pump 20, which discharges through line 21 and valve 22 into line 15 where the cooling oil commingles with the conversion products, as previously described.

Vaporizing and separating chamber 17 is preferably operated at substantially the same or at a reduced pressure relative to that maintained in reaction chamber 10 and may range, for example, from 5 to 150 pounds per square inch. The mixture of cooling oil and conversion products, due to its contained heat and the reduction in pressure in chamber 17, when the latter is employed, undergoes substantial vaporization to form a non-vaporous liquid residue which contains the heavy components of both the cooling oil and conversion products and hydrocarbon vapors which contain the lighter components of both the cooling oil and conversion products. The non-vaporous liquid residue separated in chamber 17 is directed from the lower portion thereof through line 23 and valve 24 to cooling and storage or to any desired further treatment.

The hydrocarbon vapors separated in chamber 17 are directed from the upper portion thereof through line 25 and valve 26 into fractionator 27 which is preferably operated at substantially the same pressure or at a slightly reduced pressure relative to that employed in chamber 17. The hydrocarbon vapors introduced to fractionator 27 are fractionated therein to form reflux condensate and to separate fractionated vapors boiling in the range of gasoline. When heavy hydrocarbons are present in the vapors in chamber 17, the reflux condensate formed in fractionator 27 may be divided into plurality of fractions and only selected light oils returned to the cracking treatment. For example, when the 90% Engler distillation temperature of the reflux condensate collected in the lower portion of fractionator 27 is substantially higher than 700° F., all of this reflux condensate may be recovered as a product of the process or supplied to a separate mixed phase cracking system, if desired, in which case reflux condensate obtained as a side-stream from fractionator 27 may be supplied to vapor phase cracking treatment.

When all of the reflux condensate in fractionator 27 is supplied to the vapor phase cracking treatment, it may be accomplished by directing

said reflux condensate from the lower portion of fractionator 27 through line 28, valve 29, and line 30 to pump 31, which discharges through line 32 and valve 33 into line 4, for treatment as previously described. On the other hand, when the reflux condensate, removed from the lower portion of fractionator 27, contains heavy ends which render the stock unsuitable for vapor phase cracking, all of it may be recovered as a product of the process by way of line 34 and valve 35 or supplied to any desired further treatment. In this case, a lighter reflux condensate obtained as a side-stream from fractionator 27 may be supplied to the cracking treatment by way of line 36, line 38, valve 37, pump 31, line 32 and valve 33. When desired, a portion or all of the light reflux condensate removed from fractionator 27 by way of line 36 may be recovered as a product of the process by withdrawing the same through valve 38.

Fractionated vapors separated in fractionator 27 are directed through line 39 and valve 40 to cooling and condensation in condenser 41. Distillate, together with undissolved and uncondensed gases, is directed from condenser 41 through line 42 and valve 43 into receiver 44 where the distillate and undissolved and uncondensed gases are collected and separated. A portion of the distillate collected and separated in receiver 44 may be returned to the upper portion of fractionator 27, by well known means not shown, as a refluxing and cooling medium.

The remaining distillate in receiver 44 is directed from the lower portion thereof through line 45 and valve 46 to pump 47, which discharges through line 48 and valve 49 into absorber 50, while the undissolved and uncondensed gases collected in receiver 44 are directed from the upper portion thereof through line 143 and valve 144 to compressor 145, which discharges through line 146 and valve 147 likewise into absorber 50. Absorber 50 is operated at a superatmospheric pressure on the order of 100 to 300 pounds or more per square inch and is preferably provided with a means for reboiling the liquid collected in the lower portion thereof. Reboiling, in the case here illustrated, may be accomplished by passing a suitable heating medium through closed coil 51 in indirect heat exchange relationship with the liquid within absorber 50. Gases and vapors rising in absorber 50 are contacted with a suitable absorption medium, introduced as hereinafter described, to separate a methane-hydrogen fraction and to dissolve and condense the heavier components of the gases and vapors. The methane-hydrogen fraction separated in absorber 50 is directed from the upper portion thereof through line 52 and valve 53 into line 130, for use as hereinafter described.

The liquid from absorber 50, comprising the distillate introduced thereto and an absorber oil containing dissolved and condensed gases, is directed through line 54 and valve 55 to pump 56, which discharges through line 57 and valve 58 into depropanizer 59. Depropanizer 59 is operated at a superatmospheric pressure on the order of 200 to 400 pounds or more per square inch and is provided with a closed coil 60 through which a suitable reboiling medium may be circulated. A normally gaseous hydrocarbon fraction containing substantially only C₂ and C₃ hydrocarbons is separated from the heavier normally gaseous hydrocarbons and the liquid hydrocarbons in depropanizer 59. The C₂ and C₃ fraction is directed from the upper portion of depropanizer

59 through line 61 and valve 62 to pump 63, which discharges through line 64 and valve 65, the C₂-C₃ fraction commingled with a residual C₄ fraction, separated as hereinafter described, and the mixture subjected to pyrolytic treatment in heating coil 11, as previously described.

Liquid, together with dissolved and condensed gases removed from the lower portion of depropanizer 59, is directed through line 66 and valve 67 to pump 68, which discharges through line 69 and valve 70 into debutanizer 71. Debutanizer 71 is operated at a superatmospheric pressure on the order of 25 to 200 pounds or more per square inch and is equipped with a closed coil 72 through which a heating medium may be circulated for reboiling the lower portion thereof. Debutanizer 71 may be operated so that substantially all of the C₄ normally gaseous hydrocarbons are separated from the mixture introduced thereto or, when desired, since the mixture is essentially gasoline boiling range hydrocarbons and C₄ gaseous hydrocarbons it may be operated so that distillate collected in the lower portion thereof contains sufficient C₄ hydrocarbons for the vapor pressure requirements of the distillate recovered in a subsequent separating stage of the process. The distillate collected in the lower portion of debutanizer 71, either substantially free of C₄ gaseous hydrocarbons or containing a sufficient amount for vapor pressure requirements, is directed through line 73 and valve 74 to pump 75, which discharges through line 76 and valve 77 into fractionator 78.

Fractionator 78 is operated at a pressure ranging, for example, from substantially atmospheric to 100 pounds or more per square inch and is provided with a suitable means for reboiling the lower portion thereof, such as closed coil 79. The material introduced to fractionator 78 is separated by fractionation into a light gasoline and a heavy gasoline, the former being removed as vapors and the latter as reflux condensate. Vapors separated in fractionator 78 are directed from the upper portion thereof through line 80 and valve 81 to cooling and condensation in condenser 82. Distillate, together with whatever undissolved and uncondensed gases that may be present, is directed from condenser 82 through line 83 and valve 84 into receiver 85. When undissolved and uncondensed gases are present, the same may be removed from the upper portion of receiver 85 through line 86 and valve 87. Light gasoline collected in the lower portion of receiver 85 is removed therefrom by way of line 88 and valve 89 and recovered as a product of the process.

Heavy gasoline collected in the lower portion of fractionator 78 is directed through line 90 and valve 91 to pump 92. Pump 92 discharges through line 93 and a portion of the heavy gasoline is directed through valve 94 into cooler 95 where it is cooled by indirect heat exchange with a cooling medium introduced to cooler 95 by way of closed coil 96. Cooled heavy gasoline is directed from cooler 95 through line 97 and valve 98 to the upper portion of absorber 50 for use as an absorption oil, as previously described. The residual portion of the heavy gasoline in line 93 is directed through line 99 and valve 100, commingled with the light gasoline from receiver 85, or recovered separately as a product of the process.

The C₄ fraction separated in debutanizer 71 is directed from the upper portion thereof through line 101 and valve 102 to compressor 103, which discharges through line 104 and valve 105 into

heating coil 106. The C₄ hydrocarbons in passing through heating coil 106 are raised to the desired polymerizing temperature by means of heat supplied from furnace 107 and are discharged therefrom through line 108 and valve 109 into reactor 110 where they are subjected to contact with a polymerizing catalyst selected to effect substantial polymerization of the iso and normal butenes introduced thereto into iso-octenes.

Sulfuric acid and phosphoric acid-containing catalysts are the preferred catalysts in the polymerization treatment, however, since sulfuric acid is more selective to the polymerization of iso-butenes and since temperatures and pressures when using phosphoric acid-containing catalysts may be selected to effect substantial conversion of both iso and normal butenes, the phosphoric acid-containing catalyst is therefore the preferred catalyst. The phosphoric acid-containing catalyst consists in general of a mixture of a relatively inert carrier such as kieselguhr impregnated with the ortho or pyrophosphoric acid and is preferably precalcined before using. Polymerizing temperatures in the approximate range of 150 to 450° F. and superatmospheric pressures ranging, for example, from 800 to 1300 pounds per square inch may be employed when using the phosphoric acid-containing catalyst.

Reactor 110 is preferably of the type which employs a plurality of relatively small diameter tubes containing the polymerizing catalyst, the tubes being surrounded by a suitable cooling medium. The invention, however, is not limited to any specific type of reactor but may employ various other types, known to those skilled in the art, within its broad scope. Preferably and in order to obtain best results, a plurality of reactors is employed, connected in series with provisions for segregating one or more reactors from the group for the renewal of catalysts while the polymerizing treatment is being accomplished in the other or others, although only one is shown in the accompanying drawing.

The reaction products from reactor 110 are directed through line 111 and valve 112 into fractionator 113, operated at a superatmospheric pressure on the order of substantially atmospheric to 100 pounds or more per square inch, while the normally gaseous hydrocarbons are separated by fractionation from the normally liquid hydrocarbons and the latter further separated into an iso-octene fraction and a heavy polymer fraction. When desired, a portion or all of the normally gaseous hydrocarbons separated in fractionator 113 may be directed through line 114 and valve 115 and into line 64, commingling therein with the C₂-C₃ fraction, as previously described, or, when desired, a portion or all may be recovered by way of lines 114 and 116 and valve 117 and used for raising the vapor pressure of the distillate recovered from receiver 35, and the iso-octene recovered as hereinafter described. Preferably, however, only the amount required for raising the vapor pressure of the distillates is removed from fractionator 113 and the residual portion subjected to pyrolytic treatment, as previously described. Heavy polymers, comprising principally trimers and heavier of the butenes, are removed from the lower portion of fractionator 113 by way of line 118 and valve 119, cooled and recovered as a product of the process or, when desired, this material may be supplied to the thermal cracking treatment for conversion to lower boiling hydrocarbons.

The iso-octenes separated as an intermediate

fraction in fractionator 113 are directed through line 120 and valve 121 into pump 122, which discharges through line 123 and valve 124 into heat exchanger 125. Heat exchanger 125 may be operated either as a heater or a cooler depending upon the heat requirements in the hydrogenation reaction which follows. The heating or cooling medium may be introduced to heat exchanger 125 by way of line 126 and valve 127 and withdrawn therefrom by way of line 128 and valve 129. The iso-octene fraction at the desired temperature is directed from heat exchanger 125 through line 130 and valve 131, commingling with the methane-hydrogen fraction, as previously described, and the mixture supplied to reactor 132. Reactor 132 may be of substantially the same design as reactor 110, however, as was previously mentioned, various other types of reactors may be employed.

Hydrogenation in reactor 132 may be accomplished in the presence of a catalyst which in the preferred embodiment of the invention consists of nickel on relatively porous particles of a relatively inert siliceous carrier, such as kieselguhr. The catalysts may be produced by precipitating nickel carbonate on kieselguhr, pressing into pills, drying and reducing directly with hydrogen at a temperature of 750° F. However, other hydrogenating catalysts, well known in the art, such as, for example, the oxides of chromium, molybdenum, and tungsten may be employed, when desired. Temperatures ranging, for example, from 250 to 450° F. and superatmospheric pressures in the approximate range of 15 to 200 pounds or more per square inch may be employed when using a nickel catalyst.

The hydrogenated products, together with the unused excess hydrogen, are directed from reactor 132 through line 133 and valve 134 to cooling and condensation in condenser 135. Distillate comprising substantially iso-octane, together with the undissolved and uncondensed gases from condenser 135, is directed through line 136 and valve 137 into receiver 138 for collection and separation. Unused hydrogen, together with any normally gaseous hydrocarbons collected and separated in receiver 138, is removed from the upper portion thereof by way of line 139 and valve 140 and returned to reactor 132, by well known means not shown, for reuse or recovered as a product of the process. The iso-octane collected in the lower portion of receiver 138 is removed therefrom by way of line 141 and valve 142 and recovered as a product of the process.

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

Combined feed, comprising a 33° A. P. I. gravity Mid-Continent gas-oil and reflux condensate, formed as hereinafter described, was subjected to vapor phase cracking treatment in a heating coil at a temperature of 1025° F. and at an outlet pressure of approximately 75 pounds per square inch. Concurrently therewith, a gas fraction, comprising essentially C₂, C₃, and substantially paraffinic C₄ hydrocarbons formed in the process, was subjected to pyrolytic treatment in a separate heating coil at a temperature of 1075° F. and at a pressure of approximately 800 pounds per square inch. The conversion products from both heating coils were commingled and the mixture subjected to prolonged conversion treatment in a reaction chamber operated at a superatmospheric pressure substantially the same as that

employed on the outlet of the vapor phase cracking coil.

The conversion products from the reaction chamber were cooled to arrest the cracking reaction by commingling therewith a 25° A. P. I. gravity Mid-Continent reduced crude oil and the mixture supplied to a vaporizing and separating zone operated at a superatmospheric pressure of approximately 50 pounds per square inch. Non-vaporous liquid residue was separated from the vaporous components and the mixture supplied to the vaporizing and separating zone and the former recovered as a product of the process. The vaporous components were subjected to fractionation at a superatmospheric pressure substantially the same as that maintained in the vaporizing and separating zone to form light and heavy reflux condensates and to separate fractionated vapors boiling in the range of gasoline. The heavy reflux condensate was subjected to mixed phase thermal cracking treatment in a separate system. The light combined feed was commingled with the gas-oil charging stock and subjected to vapor phase cracking treatment, as previously described.

Fractionated vapors were separated into a non-condensable gas fraction comprising essentially hydrogen and methane, a C₂-C₃ fraction, a C₄ fraction, and a gasoline fraction, the latter being recovered as a product of the process. The C₂-C₃ fraction was subjected to pyrolytic treatment, as previously described.

The C₄ fraction was subjected to selective polymerization treatment in the presence of a phosphoric acid-containing catalyst at a temperature of 250° F. and at a superatmospheric pressure of 1000 pounds per square inch to form iso-octenes and iso- and normal butenes. Products from the polymerization treatment were fractionated at a superatmospheric pressure of approximately 5 pounds per square inch to separate the residual C₄ fraction from the normally liquid polymers and in addition to separate said normally liquid polymers into an iso-octene fraction and a hydrogen-methane fraction, the latter being recovered as a product of the process. A residual C₄ fraction was commingled with the C₂-C₃ fraction and subjected to pyrolytic treatment in commingled state therewith. The iso-octene fraction was subjected to hydrogenation treatment in the presence of a nickel catalyst at a temperature of 275° F. and at a superatmospheric pressure of approximately 25 pounds per square inch, the hydrogen contained in the hydrogen-methane fraction being used in the hydrogenation treatment. The products from the hydrogenation treatment were subjected to cooling and condensation, and the resulting gas and liquid collected and separated.

This operation yielded approximately 46.5% of 75 octane gasoline, 3.1% of iso-octane having an octane rating of approximately 96, 18.0% of heavy reflux condensate, and 21.3% of non-vaporous liquid residue.

The yields above stated correspond to volume per cent of the total charge, the loss corresponding to 100% minus the stated volume yields being attributed to coke and gas.

I claim as my invention:

1. A process for the production of motor and aviation gasolines, which comprises subjecting a hydrocarbon oil to thermal cracking treatment in substantially the vapor phase to effect substantial conversion thereof into gas, gasoline, and intermediate conversion products, returning

the intermediate conversion products to said thermal cracking treatment, recovering said gasoline, separating said gas into a hydrogen-methane fraction, a two and three carbon atom fraction, and a four carbon atom fraction, subjecting said two and three carbon atom fraction, together with residual four carbon atom hydrocarbons separated in a subsequent stage to pyrolytic treatment and combining the pyrolytic polymers and gases produced therein with the products of said cracking treatment, subjecting said four carbon atom fraction to polymerization treatment to effect substantial polymerization of the olefins to iso-octenes, commingling the residual four carbon atom fraction from said polymerization treatment with said two and three carbon atom fraction, as aforesaid, subjecting the iso-octenes from said polymerization treatment to hydrogenation treatment with hydrogen of said hydrogen-methane fraction and recovering therefrom iso-octane.

2. A process for the production of motor and aviation gasolines, which comprises subjecting combined feed comprising charging oil and reflux condensate, formed as hereinafter set forth, to thermal cracking treatment in substantially the vapor phase, concurrently therewith subjecting two and three carbon atom and four carbon atom hydrocarbons formed in the process to pyrolytic treatment, commingling the conversion products from both treatments and separating non-vaporous liquid residue from the vaporous components of the mixture of conversion products, recovering said non-vaporous liquid residue, fractionating said vaporous components to form reflux condensate and to separate fractionated vapors, commingling at least a portion of said reflux condensate with said charging oil to form combined feed, as aforesaid, separating said fractionated vapors into a non-condensable gas fraction comprising essentially hydrogen and methane, a two and three carbon atom fraction, a four carbon atom fraction, and a gasoline fraction, recovering the latter, supplying said two and three carbon atom fraction in commingled state with the residual four carbon atom fraction, separated as hereinafter set forth to said pyrolytic treatment, subjecting said four carbon atom fraction to polymerization treatment to effect polymerization of the olefins contained therein to iso-octenes, separating the polymerization products into a residual four carbon atom fraction, an iso-octene fraction, and a heavy polymer fraction, recovering the latter, commingling said residual four carbon atom fraction with the two and three carbon atom fraction, as aforesaid, subjecting said iso-octene fraction to hydrogenation treatment in commingled state with said non-condensable gas fraction and recovering therefrom iso-octane.

3. The process claimed in claim 2 wherein the heavier portion of the reflux condensate formed in fractionating the vaporous components is recovered and only the light reflux condensate is subjected to the thermal cracking treatment.

4. A process for the production of motor and aviation gasolines, which comprises subjecting combined feed comprising charging oil and reflux condensate, formed as hereinafter set forth, to thermal cracking treatment in substantially the vapor phase, concurrently therewith subjecting two carbon atom, three carbon atom, and four carbon atom hydrocarbons formed in the process to pyrolytic treatment, commingling the conversion products from said thermal cracking

and said pyrolytic treatments and subjecting the mixture to prolonged conversion treatment in a reaction chamber, cooling the conversion products from said reaction chamber by commingling therewith a suitable cooling oil, separating non-vaporous liquid residue from the vaporous components of the mixture of conversion products and cooling oil, recovering said non-vaporous liquid residue, fractionating said vaporous components to form reflux condensate and to separate fractionated vapors, commingling at least a portion of said reflux condensate with said charging oil to form combined feed, as aforesaid, separating said fractionated vapors into a non-condensable gas fraction comprising essentially hydrogen and methane, a two and three carbon atom fraction, a four carbon atom fraction, and a gasoline fraction, recovering the latter, supplying said two and three carbon atom fraction in commingled state with the residual four carbon atom fraction, separated as hereinafter set forth, to said pyrolytic treatment, subjecting said four carbon atom fraction to polymerization treatment to effect polymerization of the olefins contained therein to iso-octenes, separating the polymerization products into a residual four carbon atom fraction, an iso-octene fraction, and a heavy polymer fraction, recovering the latter, commingling said residual four carbon atom fraction with the two and three carbon atom fraction, as aforesaid, subjecting said iso-octene fraction to hydrogenation treatment in commingled state with said non-condensable gas fraction and recovering therefrom iso-octane.

5. A process for the production of motor and aviation gasoline, which comprises subjecting combined feed comprising charging oil and reflux condensate, formed as hereinafter set forth, to thermal cracking treatment in substantially the vapor phase, concurrently therewith subjecting two carbon atom, three carbon atom and four carbon atom hydrocarbons formed in the process to pyrolytic treatment, commingling the conversion products from said thermal cracking and said pyrolytic treatments and subjecting the mixture to prolonged conversion treatment in a reaction chamber, cooling the conversion products from said reaction chamber by commingling therewith a suitable cooling oil, separating non-vaporous liquid residue from the vaporous components of the mixture of conversion products and cooling oil, recovering said non-vaporous liquid residue, fractionating said vaporous components to form reflux condensate and to separate fractionated vapors, commingling at least a portion of said reflux condensate with said charging oil to form combined feed, as aforesaid, cooling and condensing said fractionated vapors to form distillate and gas and subjecting the resulting distillate and gas to absorption and successive fractionations to separate a non-condensable gas fraction, consisting essentially of hydrogen and methane, a two and three carbon atom fraction, a four carbon atom fraction, and a gasoline fraction, recovering the latter, supplying said two and three carbon atom fraction in commingled state with the residual four carbon atom fraction, separated as hereinafter set forth, to said pyrolytic treatment, subjecting said four carbon atom fraction to polymerization treatment to effect polymerization of the olefins contained therein to iso-octenes, separating the polymerization products into a residual four carbon atom fraction, an iso-octene fraction, and a heavy polymer fraction, recovering the latter,

commingling said residual four carbon atom fraction with the two and three carbon atom fraction, as aforesaid, subjecting said iso-octene fraction to hydrogenation treatment in commingled state with said non-condensable gas fraction and recovering therefrom iso-octane.

6. A process for the production of motor and aviation gasoline, which comprises subjecting combined feed comprising charging oil and reflux condensate, formed as hereinafter set forth, to thermal cracking treatment in substantially the vapor phase, concurrently therewith subjecting two, three, and four carbon atom hydrocarbons formed in the process to pyrolytic treatment, commingling the conversion products from said thermal cracking and said pyrolytic treatments and subjecting the mixture to prolonged conversion treatment in a reaction chamber, cooling the conversion products from said reaction chamber by commingling therewith a suitable cooling oil, separating non-vaporous liquid residue from the vaporous components of the mixture of conversion products and cooling oil, recovering said non-vaporous liquid residue, fractionating said vaporous components to form reflux condensate and to separate fractionated vapors, commingling at least a portion of said reflux condensate with said charging oil to form combined feed, as aforesaid, cooling and condensing said fractionated vapors to form distillate and gas and subjecting the resulting distillate and gas to absorption and successive fractionations to separate a non-condensable gas fraction consisting essentially of hydrogen and methane, a two and three carbon atom fraction, a four carbon atom fraction, and a gasoline fraction, recovering the latter, supplying said two and three carbon atom fraction in commingled state with the residual four carbon atom fraction, separated as hereinafter set forth, to said pyrolytic treatment, subjecting said four carbon atom fraction to polymerization treatment in the presence of a phosphoric acid-containing catalyst to effect polymerization of the olefins contained therein to iso-octenes, separating the polymerization products into a residual four carbon atom fraction, an iso-octene fraction, and a heavy polymer fraction, recovering the latter, commingling said four carbon atom fraction with the two and three carbon atom fraction, as aforesaid, subjecting said iso-octene fraction to hydrogenation treatment in commingled state with said non-condensable gas fraction in the presence of a nickel-containing catalyst and recovering therefrom iso-octane.

7. A process for the production of motor and aviation gasoline, which comprises subjecting combined feed comprising charging oil and reflux condensate, formed as hereinafter set forth, to thermal cracking treatment in substantially the vapor phase, concurrently therewith subjecting two, three, and four carbon atom hydrocarbons formed in the process to pyrolytic treatment, commingling the conversion products from said thermal cracking and said pyrolytic treatments and subjecting the mixture to prolonged conversion treatment in a reaction chamber, cooling the conversion products from said reaction chamber by commingling therewith a suitable cooling oil, separating non-vaporous liquid residue from the vaporous components of the mixture of conversion products and cooling oil, recovering said non-vaporous liquid residue, fractionating said vaporous components to form reflux condensate and to separate fractionated vapors, commingling at least a portion of said reflux condensate with said

charging oil to form combined feed, as aforesaid, cooling and condensing said fractionated vapors to form distillate and gas and subjecting the resulting distillate and gas to absorption and successive fractionation to separate a non-condensable gas fraction consisting essentially of hydrogen and methane, a two and three carbon atom fraction, a four carbon atom fraction, and a gasoline fraction, recovering the latter, supplying said two and three carbon atom fraction in commingled state with the residual four carbon atom fraction, separated as hereinafter set forth, to said pyrolytic treatment, subjecting said four carbon atom fraction to polymerization treatment in the presence of a phosphoric acid-containing catalyst at a temperature of from 150 to 450° F. and at a superatmospheric pressure of from 800 to 1300 pounds per square inch to effect polymerization of the olefins contained therein to iso-octenes, separating the polymerization products into a residual four carbon atom fraction, an iso-octene fraction, and a heavy polymer fraction, recovering the latter, commingling said residual four carbon atom fraction with the two and three carbon atom fraction, as aforesaid, subjecting said iso-octene fraction to hydrogenation treatment in commingled state with said non-condensable gas fraction in the presence of a nickel-containing catalyst at a temperature of from 250 to 450° F. and at a superatmospheric pressure of from 15 to 200 pounds per square inch and recovering therefrom iso-octane.

8. A process for the production of motor and aviation gasolines, which comprises subjecting combined feed comprising charging oil and reflux condensate, formed as hereinafter set forth, to thermal cracking treatment in substantially the vapor phase at a temperature of from 975 to 1150° F. and at a superatmospheric pressure of from 5 to 150 pounds per square inch, concurrently therewith subjecting two, three and four carbon atom hydrocarbons formed in the process to pyrolytic treatment at a temperature of from 900 to 1400° F. and at a superatmospheric pressure of from 500 to 3000 pounds per square inch, commingling the conversion products from said thermal cracking and said pyrolytic treatments and subjecting the mixture to prolonged conversion treatment in a reaction chamber, cooling the conversion products from said reaction chamber by commingling therewith a suitable cooling oil,

separating non-vaporous liquid residue from the vaporous components of the mixture of conversion products and cooling oil, recovering said non-vaporous liquid residue, fractionating said vaporous components to form reflux condensate and to separate fractionated vapors, commingling at least a portion of said reflux condensate with said charging oil to form combined feed, as aforesaid, cooling and condensing said fractionated vapors to form distillate and gas and subjecting the resulting distillate and gas to absorption and successive fractionation to separate a non-condensable gas fraction consisting essentially of hydrogen and methane, a two and three carbon atom fraction, a four carbon atom fraction, and a gasoline fraction, recovering the latter, supplying said two and three carbon atom fraction in commingled state with the residual four carbon atom fraction, separated as hereinafter set forth, to said pyrolytic treatment, subjecting said four carbon atom fraction to polymerization treatment in the presence of a phosphoric acid-containing catalyst at a temperature of from 150 to 450° F. and at a superatmospheric pressure of from 800 to 1300 pounds per square inch to effect polymerization of the olefins contained therein to iso-octenes, separating the polymerization products into a residual four carbon atom fraction, an iso-octene fraction, and a heavy polymer fraction, recovering the latter, commingling said residual four carbon atom fraction with the two and three carbon atom fraction, as aforesaid, subjecting said iso-octene fraction to hydrogenation treatment in commingled state with said non-condensable gas fraction in the presence of a nickel-containing catalyst at a temperature of from 250 to 450° F. and at a superatmospheric pressure of from 15 to 200 pounds per square inch and recovering therefrom iso-octane.

9. The process claimed in claim 8 wherein cooling oil comprises essentially a high-boiling hydrocarbon oil.

10. The process claimed in claim 8 wherein the heavy portion of the reflux condensate formed in fractionating the vaporous components is recovered and only the light reflux condensate subjected to thermal cracking treatment.

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