

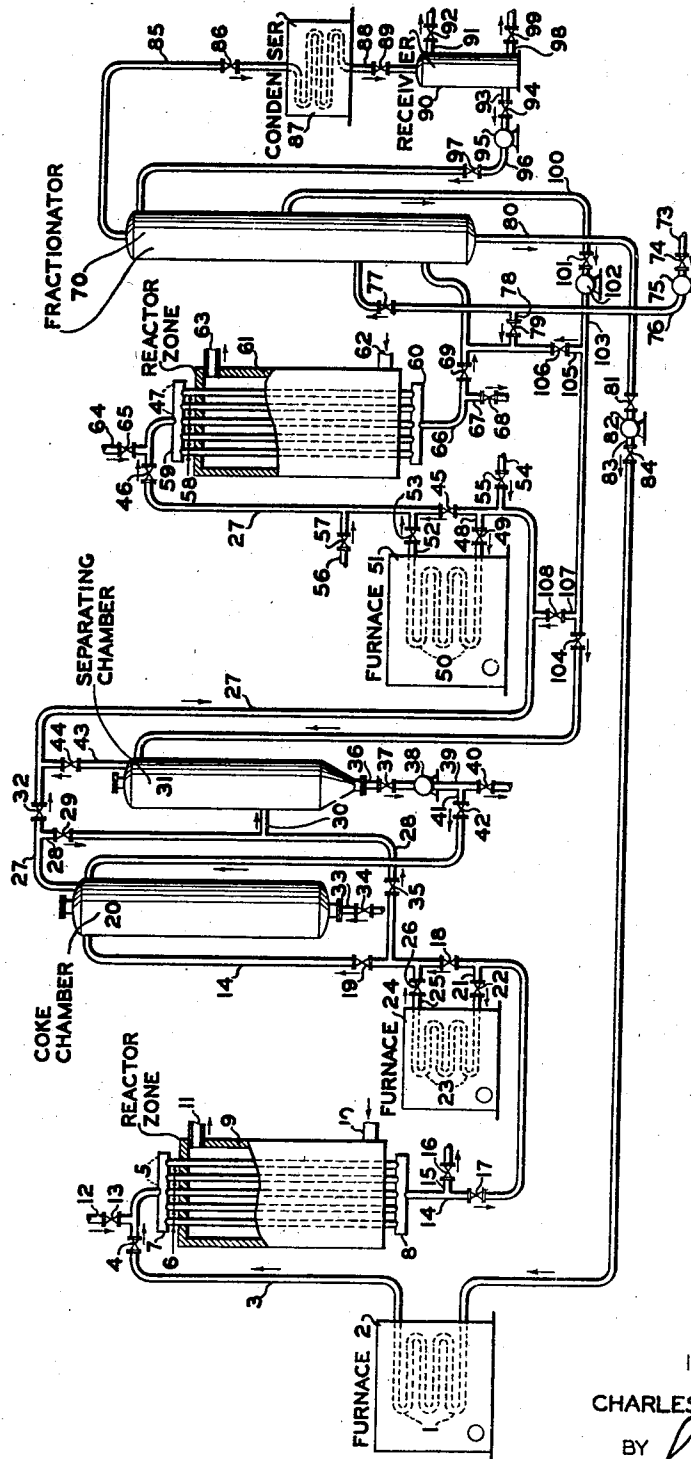
**Sept. 1, 1942.**

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**2,294,584**

# CATALYTIC TREATMENT OF HYDROCARBON OIL

Filed Jan. 30, 1939



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## UNITED STATES PATENT OFFICE

2,294,584

## CATALYTIC TREATMENT OF HYDROCARBON OILS

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Application January 30, 1939, Serial No. 253,627

8 Claims. (Cl. 196-49)

This invention relates particularly to the manufacture of gasoline from hydrocarbon oils heavier than gasoline and is more specifically concerned with a process which provides for converting hydrocarbon oils of a higher average boiling point and a higher specific gravity than gasoline, and which contain hydrocarbons that are not readily vaporized under the conditions employed when catalytically cracking clean vaporous stocks, to lower specific gravity and lower average boiling point hydrocarbons than the charging stock and/or gasoline of good antiknock properties, and, in addition, gases relatively rich in polymerizable olefins.

The charging stock for catalytic cracking processes preferably comprises a gas-oil or a readily vaporizable hydrocarbon oil because it has been found desirable to carry the reaction out substantially under vapor phase conditions. In other processes the charging stock, which contains relatively high-boiling, non-vaporizable fractions, is commingled with the conversion products from the catalytic cracking reaction as cooling oil followed by fractionation of the commingled materials to separate a gasoline product, an intermediate fraction which may be substantially completely vaporized and which is good starting material for catalytic cracking in the vapor phase, and non-vaporizable residue. In the latter process, however, the yields obtained do not correspond to the optimum yields from a given charging stock, and it is the purpose of this invention to improve the yields of gasoline by subjecting the relatively high-boiling, non-vaporizable hydrocarbon fractions in the charging stock, together with non-vaporizable conversion products produced in the process, to catalytic conversion in the liquid phase.

This invention, therefore, provides an improved process for catalytically cracking high-boiling hydrocarbons in two stages, the first stage being carried out substantially under liquid phase conditions and the second stage substantially under vapor phase conditions with provision for separation of non-vaporous residue from vaporous components between the two stages.

It has been found that hydrocarbon oils containing substantial quantities of relatively high-boiling fractions may be converted to oils of a relatively lower average boiling point and lower specific gravity than the charging stock by catalytic means, and that the catalytic reaction may be so regulated that relatively small quantities of carbon are deposited upon the catalyst in the first stage. This may be accomplished by sub-

jecting the charging stock substantially under liquid phase conditions to contact with a cracking catalyst at a lower temperature and a higher superatmospheric pressure relative to the temperature and pressure employed when catalytically cracking clean readily vaporizable stocks so that the catalyst is continuously subjected to the washing action of the liquid materials while the processing is taking place and the amount of carbonaceous materials deposited upon the catalyst is substantially reduced with provision for removing the coke forming materials in either a coke chamber or a separating chamber or both after the first stage and further provisions made for catalytically cracking the clean vaporous stocks produced in the first stage in a second stage. In addition, it has been found that hydrocarbon oils subjected to such treatment yield substantially more light oils and/or gasoline than is obtained in any of the known processes which operate on the vaporous fractions obtained from the hydrocarbon charging stock only. The present invention further provides for recycling a portion of the relatively high-boiling liquid conversion products produced in the process by commingling the same with the charging stock in order to materially reduce the coking tendency of the charging stock.

In one specific embodiment the present invention comprises subjecting relatively heavy reflux condensate to catalytic cracking in substantially liquid phase in a primary step, further treating the products to separate vapors from the non-vaporous residue and recovering the latter as coke, subjecting said vapors to catalytic cracking in a second stage, cooling the cracked products from the second stage by introducing relatively light reflux condensate thereto, subjecting the mixture of cracked products and cooling oil to fractionation along with charging oil to produce overhead vapors of gasoline boiling range which are condensed and collected, relatively light reflux condensate used as said cooling oil, and heavy reflux condensate cracked in said primary stage.

The outline of the process given in the preceding paragraph will be amplified in the following description to indicate its important features in greater detail by describing the characteristic operations in connection with the attached diagrammatic drawing. The drawing illustrates one specific form of apparatus in which the process of the invention may be conducted. However, the application of the features of the invention to other specific types of apparatus will be readily

apparent to those familiar with the catalytic cracking art, and the obvious departures from the modifications and the specific embodiment of the invention, above described, are entirely within the scope of the broader features of the process herein provided.

The accompanying diagrammatic drawing illustrates one specific form of apparatus in which the process of the invention may be successfully conducted.

Referring to the drawing, heating coil 1 is disposed within a furnace 2 by means of which the required heat is supplied to the commingled oils passing through the heating coil to bring them to the desired temperature, preferably at a substantial superatmospheric pressure. In the particular case here illustrated, it is preferred that the heat supplied to the commingled oils passing through heating coil 1 be sufficient to raise them to the desired temperature but that the time required in reaching such a temperature be relatively rapid in order to suppress any thermal cracking reaction.

The heated products, substantially in the liquid phase, are discharged from heating coil 1 through line 3 and valve 4 into catalytic reactor 5 wherein they are contacted with a cracking catalyst disposed therein.

Preferably and in the case here illustrated, catalytic reactor 5 comprises a plurality of small diameter reactor tubes 6 connected in parallel between upper and lower headers 7 and 8 and is disposed within a heating or cooling zone 9. Catalytic cracking is an endothermic reaction requiring heat and, therefore, in order to obtain best results heat must be supplied to the material undergoing conversion within reactor 5. It has been found that best results are usually obtained when employing fluid heating means which preferably comprises hot combustion gases which may be introduced to zone 9 through duct 10, passed in indirect heat exchange relationship with the materials passing through reactor tubes 6, after which they are discharged from the upper portion of zone 9 through duct 11.

In catalytic endothermic reactions, such as catalytic cracking, carbon deposits upon the catalyst at a relatively rapid rate and tends to decrease the catalyst activity, this fact being even more apparent when the charging stock comprises relatively high-boiling, non-vaporizable residual hydrocarbon oils. In order to obtain best results, relatively short operating periods are employed, i. e., the catalysts are subjected to contact with the materials undergoing conversion for a relatively short time and are then reactivated in approximately the same length of time. In this case it is preferred that a plurality of reactors be employed, each disposed within a separate heating or cooling zone, and in order that the operation may be made continuous, reactivation may be accomplished in some of the reactors while the others are processing.

Although I have found it advantageous to employ a reactor of the type described above, various other kinds, such as, for example, the chamber type, may be employed without departing from the broad scope of the invention. Catalysts which have been found to be highly efficient in the catalytic cracking of hydrocarbon oils consist in general of uniform sized pellets of specially prepared silica composited with the alumina, the amount of alumina being varied to suit requirements depending upon the stock to be treated and the operating conditions employed. As a

rough average, good results are usually obtained, for example, when employing silica composited with 15% alumina. This alumina is varied for best results under specific conditions over a relatively wide range, for example, from 2% to 50% or alumina may be employed as the major ingredient and the silica varied over substantially the same range as the alumina, i. e., 2% to 50%. Catalysts of this character may be initially prepared in any of several different manners and subsequently dried. The preferred catalyst is prepared by precipitating silica hydrogel from a solution of sodium silicate by acidifying with an acid, such as hydrochloric acid, for example, subsequently treating and washing the silica hydrogel to remove substantially all of the alkali metal ions, suspending the purified silica hydrogel in a solution of aluminum salts and depositing the alumina hydrogel upon the suspending silica by the addition of volatile basic precipitants, such as, for example, ammonium hydroxide, ammonium carbonate, or ammonium sulphide. After the alumina hydrogel has been deposited upon the purified hydrated silica hydrogel, the material is dried, formed into pellets, when desired, and calcined at a temperature of approximately 850 to 1000° F.

Although the present process has been found to operate very effectively in catalytically cracking petroleum oils when employing a catalyst consisting of silica composited with 15% alumina, the process is not limited to this particular composition of catalyst but may employ other composite catalysts of a refractory character, such as, for example, silica composited with a component selected from the group comprising zirconia, vanadia, alumina-zirconia, or aluminathoria, and acid-treated clays may also be employed. The catalysts referred to above are not exactly equivalent in their reaction and are not to be considered as absolute substitutes one for the other, which fact will be more or less apparent to those skilled in the art.

In the particular case here illustrated, when the catalysts are reactivated the flow of hydrocarbon oil is stopped and suitable reactivating gas mixtures at an elevated temperature and containing regulated quantities of oxygen are introduced to catalytic reactor 5 through line 12, valve 13, and line 3. The reactivating gases pass through reactor tubes 6, and due to oxidation the carbon deposited upon the catalysts disposed therein is caused to burn. The resulting mixture of combustion gases and reactivating gases is discharged from reactor 5 through line 14 and is directed through line 15 and valve 16 to storage or further use as a reactivating gas mixture or a portion or all may be cooled and recirculated as the reactivating gas mixture or the whole may be discharged to the atmosphere as desired. When reactivating the catalyst the reaction is exothermic and, therefore, suitable means must be employed to dissipate the heat generated therein. In this case it is preferred to employ cooled combustion gases which are supplied to zone 9 through duct 10, passing therethrough in indirect heat exchange relationship with the flow of reactivating gases in reactor tubes 6, and are discharged therefrom through duct 11. The vaporous and liquid conversion products are discharged from reactor 5 through line 14 and valve 17 and may be directed all or in part through valves 18 and 19 to coke chamber 20. However, when the conversion products from catalytic reactor 5 lack sufficient

heat to coke material deposited within coke chamber 20, additional heat may be acquired by means of furnace 24. In this case, all or a portion of the conversion products in line 14 are directed through line 21 and valve 22 to heating coil 23. Heat is supplied to the conversion products passing through heating coil 23 by means of furnace 24 and they are discharged therefrom through line 25 and valve 26 into line 14 and introduced to coke chamber 20, as previously described.

The liquid conversion products introduced to coke chamber 20 in commingled state with the vaporous conversion products are reduced to substantially dry coke therein, and the vaporous conversion products, together with the vapors evolved within coke chamber 20, are withdrawn from the upper portion thereof through line 27 and may be introduced all or in part to separating chamber 31 by way of line 28, valve 29, and line 30, or the vaporous materials may be directed through valve 32 and treated, as subsequently described.

Preferably, a plurality of coke chambers are employed, although only one is shown in the diagrammatic drawing, in order that the coking operation may be made continuous with respect to the balance of the apparatus by alternately coking and cleaning each chamber. In the case here illustrated, before coke chamber 20 is cleaned of the coke deposited therein, steam is preferably introduced through line 33 and valve 34 in order to purge the vessel of hydrocarbon vapors.

In case it is desirable to make liquid residue instead of coke, coke chamber 20 may be bypassed and the conversion products in line 14 directed through line 28, valve 35, and line 30 to separating chamber 31. The preferred method, however, consists of introducing the conversion products to coke chamber 20 and supplying the vaporous materials from coke chamber 20 to separating chamber 31. In separating chamber 31 the high-boiling, coke-forming materials carried over with the vaporous materials from coke chamber 20 are separated from the vaporous materials and collected in the bottom. The high-boiling, coke-forming materials are directed from the lower portion of separating chamber 31 through line 36 and valve 37 to pump 38 which discharges through line 39, and all or a portion of these materials may be directed through valve 40 to cooling and storage. In the preferred process, however, these materials are returned to coke chamber 20 by way of line 41 and valve 42 in order that they may be reduced to coke.

The vaporous materials separated in separating chamber 31 are withdrawn from the upper portion thereof through line 43 and are directed through valve 44 into line 27. The vaporous materials in line 27 are preferably heated to the desired reaction temperature in furnace 51, however, when and if these materials are at the desired reaction temperature they may be directed through valve 45 and valve 46 to reactor 47. Preferably, however, these vaporous materials in line 27 are subjected to heating in furnace 51, this being accomplished by directing them through line 48 and valve 49 to heating coil 50. The heated materials are discharged from heating coil 50 through line 52 and valve 53 into line 27 by means of which they are supplied to reactor 47, as previously described.

In order to maintain the charge to catalytic reactor 47 in the vapor state under the relatively

low pressure employed in this catalytic reaction, and in order to reduce the effective pressure on the hydrocarbon vapors, steam may be introduced to the vaporous products either before heating coil 50 by way of line 54 and valve 55 or after heating coil 50 by way of line 56 and valve 57.

In the case here illustrated, catalytic reactor 47 is constructed similarly to catalytic reactor 5 and consists of relatively small diameter reactor tubes 58 connected in parallel between upper and lower headers 59 and 60 and disposed within a heating or cooling zone 61. As in the case of catalytic reactor 5, the preferred form of heating the materials within catalytic reactor 47 is by fluid heating means. Hot combustion gases, comprising the fluid heating means, may be introduced to zone 61 by way of duct 62, passed in indirect heat exchange relationship with the vaporous materials passing through reactor tubes 58, and discharged from the upper portion of zone 61 by way of duct 63.

Catalysts are preferably employed in catalytic reactor 47 which have been found to be highly efficient in the catalytic cracking of hydrocarbon oil vapors to produce optimum yields of gasoline. The preferred catalysts for effecting catalytic cracking of vaporous materials consist in general of pellets or granules of the same materials as were previously described, and, also, the methods previously disclosed for preparing catalysts are employed for preparing these catalysts.

The activation of the catalysts disposed within reactor 47 is accomplished by stopping the flow of vapors to reactor 47 by means of valve 46 and introducing suitable reactivating gas mixtures at an elevated temperature and containing regulated quantities of oxygen by way of line 64, valve 65, and line 27. The reactivating gases pass through reactor tubes 57, and due to oxidation the carbon deposited upon the catalysts disposed therein is caused to burn. The resulting mixture of combustion gases and reactivating gases is discharged from reactor 47 through line 66 and is directed through line 67 and valve 68 to storage for further use or elsewhere as desired. During reactivation, in order to dissipate the heat generated in the exothermic reaction, cooled combustion gases are preferably supplied to zone 61 by way of duct 62, passed in indirect heat exchange relationship with the reactivating gases in reactor tubes 58, and discharged by way of duct 63.

In order that the catalytic cracking reaction carried out in catalytic reactor 47 may be made continuous with respect to the balance of the equipment, and because of necessity the reactors are operated on a relatively short-time schedule, a plurality of reactors are preferably employed, each disposed within a separate heating or cooling zone. In this case the reactivation is carried out in some of the reactors while the others are processing. Although the type of reactor described above has been found to have many advantages when employed in this particular process, various other types of reactors may be employed without departing from the broad scope of the invention. The conversion products discharged from catalytic reactor 47 are directed through line 66 and valve 69, cooled to a relatively low temperature by commingling with the same a suitable cooling oil and the conversion products, together with the cooling oil introduced to fractionator 70.

Charging stock for the process, preferably comprising a hydrocarbon oil heavier than gasoline, is introduced through line 73 and valve 74 to pump 75 which discharges through line 76 and all or a portion of the charging stock directed through valve 77 into fractionator 70. The preferred method, however, for introducing charging stock to the process consists in commingling at least a portion of the charging stock in line 76 with the conversion products discharged from catalytic reactor 47 in line 66 as cooling oil. This may be accomplished by directing all or a portion of the charging stock in line 76 through line 78, valve 79, and line 105 into line 66.

In fractionator 70, from the commingled conversion products and cooling oil (and when oil other than charging stock is employed as cooling oil, the charging stock), fractionated vapors of the desired end boiling point are separated from the higher boiling liquid conversion products and the higher boiling fractions of the charging stock.

Fractionated vapors of the desired end boiling point are directed from the upper portion of fractionator 70 through line 85 and valve 86 to condenser 87. The resulting gas-containing distillate, together with undissolved and uncondensed gases discharged from condenser 87, are directed through line 88 and valve 89 to receiver 90. Undissolved and uncondensed gases collected and separated in receiver 90 are directed from the upper portion thereof through line 91 and valve 92 to collection and storage or elsewhere as desired. A portion of the distillate collected and separated in receiver 90 is directed through line 93 and valve 94 to pump 95 which discharges through line 96 containing valve 97 into the upper portion of fractionating zone 72 for refluxing and cooling therein. The balance of the distillate collected and separated in receiver 90 is directed from the lower portion thereof through line 98 and valve 99 to stabilization or to storage or to further treatment as desired.

The higher boiling hydrocarbons, comprising fractions of the conversion products and fractions of the charging stock whose average boiling point is above that of the fractionated vapors, are selectively condensed as light and heavy reflux condensate in fractionator 70. The light reflux condensate is withdrawn from an intermediate point in fractionator 70 and is directed through line 100 and valve 101 to pump 102. Pump 102 discharges through line 103 and a portion of the reflux condensate in line 103 may be directed through line 105 and valve 106 and commingled with the conversion products in line 66 as cooling oil prior to their introduction to fractionator 70. The balance or all of the light reflux condensate in line 103 may, when desired, be directed through line 107 and valve 108 into line 27 for subsequent conversion in commingled state with the vaporous materials removed from separating chamber 31. Light reflux condensate is preferably employed as a refluxing and cooling medium in separating chamber 31, and this may be accomplished by directing at least a portion of the light reflux condensate in line 103 through valve 104 into the upper portion thereof.

The heavy reflux condensate collected in the lower portion of fractionator 70 is withdrawn therefrom and supplied to heating coil 1 for treatment, as previously described, by way of line 80, valve 81, pump 82, line 83, and valve 84.

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

- 5 The heater to which the heavy reflux condensate is supplied may employ an outlet temperature ranging, for example, from 700 to 1100° F. and a superatmospheric pressure of from less than 200 to 700 pounds or more per square inch.
- 10 Substantially the same conditions of temperature and pressure are maintained on the first catalytic cracking stage as are employed on the outlet of the heating coil to which the heavy reflux condensate is supplied. The coke chamber and
- 15 separator may employ a superatmospheric pressure substantially the same or somewhat reduced relative to the superatmospheric pressure employed on the outlet of the first catalytic cracking stage. The heating coil to which the clean
- 20 vaporous materials from the separator are supplied may employ an outlet temperature ranging, for example, from 800 to 1200° F. and a superatmospheric pressure of from 20 to 100 pounds or more per square inch. The conversion products
- 25 discharged from the second catalytic cracking stage are preferably cooled to a temperature ranging, for example, from 600 to 800° F. or at least to a temperature sufficiently low to substantially arrest any thermal cracking reaction. The
- 30 fractionator following the second stage may utilize a pressure substantially the same as that employed at the outlet of the second catalytic cracking stage.

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:

Heavy reflux condensate produced within the system was subjected to contact in the liquid phase with a silica-alumina cracking catalyst at a temperature of approximately 930° F. and under a superatmospheric pressure of approximately 300 pounds per square inch. The conversion products from this stage were introduced to a coking zone operated at a superatmospheric pressure of approximately 75 pounds per square inch wherein the non-vaporous residue was reduced to substantially dry coke. The vaporous materials removed from the coking zone were introduced to a separating zone, operated under substantially the same superatmospheric pressure as the coking zone, to remove entrained liquids from the vaporous materials and the former returned to the coking zone. The vaporous materials were removed from the separating zone and subjected to contact in the vapor state with a silica-alumina cracking catalyst at a temperature of approximately 900° F. and under a superatmospheric pressure of approximately 40 pounds per square inch. The conversion products from this second catalytic cracking stage were cooled to approximately 650° F. by commingling with the same light reflux condensate produced as herein-after described. The conversion products, together with the cooling oil, were introduced to a fractionator operated at substantially the same superatmospheric pressure as was employed on the outlet of the last mentioned catalytic cracking stage and was subjected to fractionation therein in commingled state with the charging stock comprising a 25° A. P. I. gravity Mid-Continent topped crude oil to separate fractionated vapors of the desired end boiling point from the higher boiling liquid conversion products and the higher boiling liquid fractions of the charging

stock and the fractionated vapors recovered as a product of the process. The higher boiling liquid conversion products and the higher boiling liquid fractions of the charging stock were selectively condensed as light and heavy reflux condensate and the latter subjected to conversion in the first mentioned catalytic cracking stage, as previously described. A portion of the light reflux condensate was commingled with the conversion products from the second mentioned cracking stage and the balance of the light reflux condensate subjected to conversion in the second mentioned catalytic cracking stage. This operation yielded approximately 65% of 81 octane number gasoline by volume of the charge and approximately 60 pounds of coke per barrel of charge.

I claim as my invention:

1. A process for the production of hydrocarbon oil of lower average boiling point than the charging stock and gas of relatively high polymerizable olefin content from hydrocarbon oil with an average boiling point above that of gas-oil, which comprises subjecting heavy reflux condensate, produced as hereinafter set forth, to contact, in the liquid phase at a temperature ranging from 700 to 1100° F. and under a superatmospheric pressure of from less than 200 to 700 pounds per square inch, with a silica-alumina cracking catalyst in a primary stage, separating the conversion products discharged from said primary stage into vaporous components and non-vaporous residue and recovering the latter as a product of the process, subjecting said vaporous components to contact, in the vapor phase at a temperature ranging from 800 to 1200° F. and a pressure of from substantially atmospheric to 100 pounds per square inch, with a silica-alumina cracking catalyst in a second stage, cooling the conversion products discharged from said second stage by commingling therewith charging stock for the process, fractionating the commingled conversion products and charging stock to separate gas and gasoline from the higher boiling hydrocarbons, recovering said gas and gasoline as products of the process, selectively condensing and collecting said higher boiling hydrocarbons as light and heavy reflux condensate, subjecting said light reflux condensate to conversion in commingled state with said vaporous components in said second stage, and subjecting said heavy reflux condensate to conversion in said first stage.

2. A process for the production of hydrocarbon oil of lower average boiling point than the charging stock and gas of relatively high polymerizable olefin content from hydrocarbon oil with an average boiling point above that of gas-oil, which comprises subjecting heavy reflux condensate, produced as hereinafter set forth, to contact, in the liquid phase at a temperature ranging from 700 to 1100° F. and under a superatmospheric pressure of from less than 200 to 700 pounds per square inch, with a silica-zirconia cracking catalyst in a primary stage, separating the conversion products discharged from said primary stage into vaporous components and non-vaporous residue and recovering the latter as a product of the process, subjecting said vaporous components to contact, in the vapor phase at a temperature ranging from 800 to 1200° F. and a pressure of from substantially atmospheric to 100 pounds per square inch, with a silica-zirconia cracking catalyst in a second stage, cooling the conversion products discharged from said second stage by commingling therewith charging stock for the

process, fractionating the commingled conversion products and charging stock to separate gas and gasoline from the higher boiling hydrocarbons, recovering said gas and gasoline as products of the process, selectively condensing and collecting said higher boiling hydrocarbons as light and heavy reflux condensate, subjecting said light reflux condensate to conversion in commingled state with said vaporous components in said second stage, and subjecting said heavy reflux condensate to conversion in said first stage.

3. A conversion process which comprises subjecting heavy hydrocarbon oil to relatively mild cracking under sufficient superatmospheric pressure to maintain a substantial portion thereof in liquid phase and in the presence of a cracking catalyst comprising silica and alumina, separating the thus treated oil into vapors and residue, subjecting the separated vapors to further catalytic cracking at higher temperature and under lower pressure than and independently of said heavy oil, fractionating the resultant conversion products to form light reflux condensate and a heavier reflux condensate, supplying said heavier reflux condensate to the first mentioned cracking step, and supplying the light reflux condensate to the second mentioned cracking step.

4. A process for the conversion of heavy hydrocarbon charging stocks which comprises subjecting heavy reflux condensate, formed as hereinafter set forth, to relatively mild cracking in a primary stage under sufficient pressure to maintain a substantial portion thereof in liquid phase and in the presence of a siliceous cracking catalyst, separating the thus treated reflux condensate into vapors and residue, subjecting the separated vapors to further catalytic cracking in a secondary stage at higher temperature and under lower pressure than and independently of the reflux condensate in the primary stage, fractionating the resultant conversion products in admixture with the charging stock for the process to separate gasoline and gas and to form a light reflux condensate and a heavier reflux condensate, supplying said heavier reflux condensate to the primary stage and supplying said light reflux condensate to the secondary stage.

5. The process as defined in claim 4 further characterized in that the charging stock is commingled with said conversion products promptly upon discharge of the latter from the secondary stage whereby to quench said products.

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

7. A conversion process which comprises subjecting heavy hydrocarbon oil to relatively mild cracking under sufficient superatmospheric pressure to maintain a substantial portion thereof in liquid phase and in the presence of a cracking catalyst comprising silica and zirconia, separating the thus treated oil into vapors and residue, subjecting the separated vapors to further catalytic cracking at higher temperature and under lower pressure than and independently of said heavy oil, fractionating the resultant conversion products to form light reflux condensate and a heavier reflux condensate, supplying said heavier reflux condensate to the first mentioned cracking step and supplying said light reflux condensate to the second mentioned cracking step.

8. The process of claim 3 further characterized in that the catalyst contains zirconia.

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