

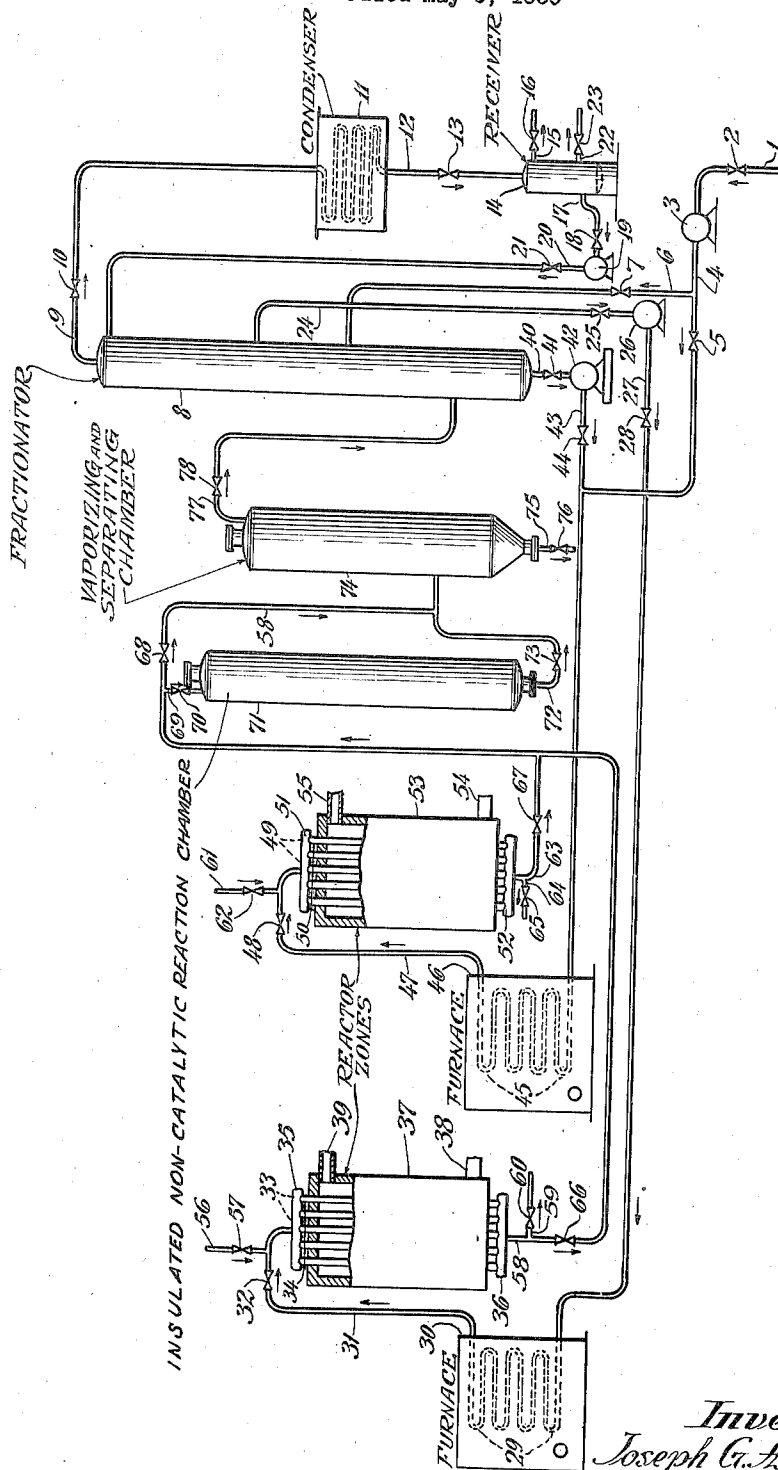
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CATALYTIC CONVERSION OF HYDROCARBON OILS

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CATALYTIC CONVERSION OF HYDRO-CARBON OILS

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3 Claims. (Cl. 196-48)

This invention relates particularly to the manufacture of gasoline from hydrocarbon oils boiling above gasoline and more specifically to a process wherein the hydrocarbon oil is selectively converted by catalytic means into gasoline of relatively high anti-knock value and valuable gases of relatively high polymerizable olefin content.

The invention specifically provides an improved method for catalytically converting fractions of the hydrocarbon oil under conditions of temperature, pressure and contact time selected to effect optimum conversion to gasoline.

One specific embodiment of the invention comprises subjecting vaporous conversion products, formed as hereinafter set forth, and hydrocarbon oil charging stock to fractionation in commingled state to separate therefrom fractionated vapors of the desired end boiling point and higher boiling hydrocarbons, separating the latter into selected relatively light and heavy fractions, subjecting the fractionated vapors to condensation, recovering and separating the distillate and gases, subjecting said relatively light and heavy fractions to separate catalytic cracking treatment under conditions best suited for the conversion of each, separating the resulting conversion products of both cracking operations into vaporous and non-vaporous components and supplying the former as the first named vaporous conversion products to the fractionating step.

The invention specifically contemplates cracking a light reflux condensate in essentially the vaporous state while separately cracking a heavy reflux condensate in either the vaporous state or in mixed phase depending upon the type of charging stock employed. For example, when the charging stock is essentially a gas-oil which may be substantially completely vaporized, both cracking operations may be performed in essentially the vaporous state, while, on the other hand, if the charging stock includes hydrocarbon oils boiling above gas-oil, the light reflux condensate may be cracked in essentially the vaporous state while the heavy reflux condensate is cracked in essentially mixed phase.

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 characteristic operations of the process 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 adaptability of the

features of the invention to use in other specific forms of cracking apparatus will be readily apparent to those familiar with the art, and the drawing should therefore not be construed as limiting the invention in its broader concepts.

Referring to the drawing, charging stock for the process, preferably comprising crude oil, reduced crude, or any fraction thereof, is directed through line 1 and valve 2 to pump 3. Pump 3 discharges through line 4, and when the charging stock comprises a hydrocarbon oil from which all the lighter components, including those boiling within the range of gas-oil, have been removed, all or a portion of it may be directed through valve 5 into line 43 and commingled therein with heavy reflux condensate, produced as hereinafter described. Preferably, however, and particularly when the charging stock comprises a wide boiling range hydrocarbon oil or a low boiling fraction thereof, it is directed through line 6 and valve 7 into fractionator 8 and is subjected to fractionation therein in commingled state with the vaporous conversion products from the process, introduced as subsequently described.

The vaporous conversion products and any charging stock supplied to fractionator 8 are therein fractionated to separate relatively light vapors and gases of the desired end boiling point from the higher boiling hydrocarbons. The fractionated vapors are directed from the upper portion of fractionator 8 through line 9 and valve 10 to cooler and condenser 11. Resulting distillate, together with undissolved and undensated gases from cooler and condenser 11, are directed through line 12 and valve 13 to receiver 14. Undissolved and undensated gases collected and separated in receiver 14 are directed from the upper portion thereof through line 15 and valve 16 to storage or elsewhere as desired. A portion of the distillate collected and separated in receiver 14 is directed from the lower portion thereof through line 17 and valve 18 to pump 19 which discharges through line 20 containing valve 21 into the upper portion of fractionator 8, wherein the distillate serves as a refluxing and cooling medium. The balance of the distillate collected and separated in receiver 14 is directed from the lower portion thereof through line 22 and valve 23 to further treatment, storage or elsewhere as desired. The higher boiling hydrocarbons separated from the fractionated vapors in fractionator 8, are fractionally condensed in this zone to form selected light and heavy reflux condensates.

The light reflux condensate is withdrawn from an intermediate point in fractionator 8 and is directed through line 24 and valve 25 to pump 26 which discharges through line 27 and valve 28 into heating coil 29. The light reflux condensate is vaporized in passing through heating coil 29 and raised to the desired temperature without substantial pyrolytic cracking thereof by means of heat supplied from furnace 30. Vaporized reflux condensate is discharged from heating coil 29 at the desired temperature and pressure and is directed through line 31 and valve 32 into catalytic reactor 33 and is contacted therein with a cracking catalyst under substantially the same conditions of temperature and pressure as those employed on the outlet of the aforementioned heating coil.

Simultaneously to the withdrawal of light reflux condensate from fractionator 8, heavy reflux condensate collected in the lower portion thereof and comprising hydrocarbon oils with an average boiling point above that of the light reflux condensate, is directed through line 40 and valve 41 to pump 42 which discharges through line 43 and valve 44 into heating coil 45, or, when charging stock is commingled with the heavy reflux condensate in line 43, the commingled oils are supplied to heating coil 45. Heating coil 45 is disposed within furnace 46 by means of which the required heat is supplied to the oil passing through the heating coil to bring it to the desired temperature without substantial pyrolytic cracking.

The heated products are discharged from heating coil 45 through line 47 and valve 48 into catalytic reactor 49 wherein they are contacted with a cracking catalyst while maintaining substantially the same conditions of temperature and pressure in this zone as those maintained on the outlet of heating coil 45.

Preferably, as in the case here illustrated, catalytic reactor 33 comprises a plurality of relatively small diameter reactor tubes 34, each containing a bed of catalytic material, not shown, capable of promoting the cracking reaction, these tubes being connected in parallel between upper and lower headers 35 and 36 and is disposed within zone 37 which is alternately employed as a heating and cooling zone. While the hydrocarbon vapors are undergoing conversion in catalytic reactor 33 some form of heating is preferably employed in zone 37, this being accomplished, in the case illustrated, by employing a fluid heating means, such as hot combustion gases, for example, which may be introduced to zone 37 through duct 38, passed in indirect heat exchange relationship with the vapors in reactor tubes 34, and discharged from zone 37 through duct 39.

Catalytic reactor 49 preferably, as here illustrated, also comprises a plurality of small diameter reactor tubes 50, each containing a bed of cracking catalyst, not shown, and connected in parallel between upper and lower headers 51 and 52 and is disposed within fluid heating and cooling zone 53. Hot combustion gases employed in zone 53 as the heating medium for the materials undergoing conversion in reactor 49 may be introduced through duct 54 and withdrawn through duct 55.

In catalytic cracking carbonaceous materials deposit upon the catalyst during its contact with the hydrocarbons undergoing cracking, and after a time the carbon deposition reaches such a point that the active surface of the catalyst exposed

to the hydrocarbons is materially reduced. Frequent reactivations after relatively short periods of operation are therefore desirable in order to maintain the catalyst in highly active state. To accomplish continuous operation when frequent reactivation of the catalyst is practiced, a plurality of reactors is employed, although only one is shown in the drawing. With a plurality of reactors, the catalyst in one or more of the reactors is subjected to reactivation, while the catalyst in another or other reactors is in contact with the stream of hydrocarbon vapors undergoing conversion. Although the type of reactor described above has been found to have many advantages when employed in this particular process, various other forms of reactors may be employed without departing from the broad scope of the invention.

The catalysts preferably employed have been found to be highly efficient in the catalytic cracking of hydrocarbon vapors or liquids and consist in general of uniform size pellets of specially prepared silica composited with alumina, the relative amounts of silica and 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 about 85% silica composited with approximately 15% alumina. This alumina percentage 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 method of preparation is to precipitate silica hydrogel from a solution of sodium silicate by acidifying, with hydrochloric acid, for example, subsequently treat and wash the silica hydrogel to remove substantially all of the alkali metal ions, suspend the purified silica hydrogel in a solution of aluminum salts and deposit the alumina hydrogel upon the suspended silica by the addition of volatile basic precipitants, such as, for example, ammonium hydroxide, ammonium carbonate, or ammonium sulfide. After the alumina hydrogel has been deposited upon the purified silica hydrogel, the material is dried, formed into pellets, and calcined at a temperature of from 850 to 1500° F. The process, however, is not limited to this particular composition of cracking catalyst but may employ other composite catalysts of a refractory character, such as, for example, silica composited with compounds selected from the group consisting of zirconia, vanadia, alumina-zirconia, or aluminathoria, and other types of cracking catalysts, such as acid treated clays, may 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 conversant with the practical aspects of catalysis.

In the case here illustrated, when the catalyst in reactor 33 is reactivated, the flow of hydrocarbon vapors is stopped and a stream of suitable reactivating gases such as combustion gases containing regulated minor quantities of oxygen is supplied to reactor 33 by way of line 56, valve 57, and line 31 at a temperature sufficient to cause combustion of the carbonaceous deposits.

The reactivating gases pass through reactor tubes 34 and, due to their temperature and the oxygen present, the carbon deposited upon the catalyst disposed therein is caused to burn and the resulting gases are discharged from reactor 33 by way of line 58, line 59, and valve 60, and may be recirculated or discharged to the atmosphere as desired, preferably after recovering heat therefrom for some useful purpose, by any well known means, not shown. Reactivation of the catalyst is an exothermic reaction and, therefore, suitable means must ordinarily be employed to dissipate excess heat evolved in the reactor during reactivation. This is accomplished in the case illustrated by directing a suitable cooling medium, such as cooled combustion gases, for example, into zone 37 by way of duct 38, passing the same in indirect heat exchange relationship with the reactivating gases in reactor tubes 34 and discharging them from reactor 37 by way of duct 39.

The catalyst in reactor 49 is reactivated in the same manner as that disposed within catalytic reactor 33 and, in this case, reactivating gases containing controlled minor amounts of oxygen are directed through line 61, valve 62, and line 47, and the resulting mixture of reactivating gases and freshly generated combustion gases formed in the burning reaction are discharged from catalytic reactor 49 through line 63, line 64, and valve 65. A fluid cooling medium may be introduced to reactor zone 53 by way of duct 54 and withdrawn by means of duct 55 during reactivation of the catalyst in reactor 49.

The conversion products from reactor 33 are withdrawn through line 58 and valve 66 and are commingled with the conversion products from reactor 49 which are directed into line 58 through line 63 containing valve 67. The stream of commingled conversion products in line 58 is preferably directed through line 69 and valve 70 into non-catalytic reaction chamber 71, which is preferably maintained under a superatmospheric pressure equivalent to or slightly less than that maintained on the outlet of catalytic reactor 33 and wherein appreciable continuous cracking of the conversion products is accomplished. Chamber 71 is preferably insulated to conserve heat, although insulation is not indicated in the drawing.

The conversion products from reactors 33 and 49 pass through substantially the entire length of reaction chamber 71 and are directed in commingled state from the lower portion of this zone through line 72 and valve 73 to vaporizing and separating chamber 74. When desired, reaction chamber 71 may be by-passed by closing valve 70 in line 69 and the conversion products in line 58 directed through valve 68 into line 72 by means of which they are introduced to separating chamber 74. Chamber 74 is preferably maintained at a substantially reduced pressure relative to that employed in chamber 71 by the regulation of valve 73 in line 72, and the reduction in pressure between these two zones is sufficient to effect substantial vaporization of existing liquid conversion products supplied to chamber 74 whereby they are reduced to a non-vapor-residue of the desired characteristics. Separation of vapor and non-vaporous residue is accomplished in chamber 74 and provision is made for removing residual liquid from the lower portion of this zone through line 75 and valve 76 to cooling and storage or elsewhere as desired.

The vaporous products supplied to and evolved in chamber 74 are directed from the upper portion of this zone through line 77 and valve 78 into fractionator 8 wherein they are subjected to fractionation to separate them into gasoline and light and heavy reflux condensate, as previously described.

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

The heating coil to which the light reflux condensate is supplied may employ an outlet temperature ranging, for example, from 800 to 1200° F. with a superatmospheric pressure of from 20 to 200 pounds or more per square inch; and substantially the same conditions of temperature and pressure may be employed in the communicating catalytic reactor, the temperature and pressure employed being correlated to maintain the oil undergoing treatment in the reactor in essentially vaporous state.

The heating coil to which the heavy reflux condensate is supplied may employ an outlet temperature ranging, for example, from 800 to 1050° F. with a superatmospheric pressure from 20 to 400 pounds per square inch, and substantially the same conditions of temperature and pressure may be employed in the communicating catalytic reactor. The reaction chamber to which the liquid and vaporous conversion products are supplied may employ substantially the same or a slightly reduced pressure relative to that employed on the outlet of the catalytic reactor to which the light reflux condensate is supplied. The vaporizing and separating chamber is preferably operated at a substantially reduced pressure relative to that employed in the reaction chamber and it may range, for example, from 20 to 100 pounds per square inch superatmospheric. The fractionating, condensing, and cracking equipment may utilize a superatmospheric pressure substantially the same as that employed in the vaporizing and separating chamber.

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:

The charging stock, comprising a 37° A. P. I. gravity Mid-Continent gas-oil, was fractionated in commingled state with vaporous conversion products to separate therefrom fractionated vapors of the desired end boiling point which were recovered as a product of the process, a light reflux condensate and a heavy reflux condensate consisting of hydrocarbons boiling above the last named fraction. The light reflux condensate was contacted with a silica-alumina cracking catalyst at a temperature of approximately 960° F. and under a superatmospheric pressure of about 100 pounds per square inch. Simultaneously the heavy reflux condensate was contacted with a silica-alumina cracking catalyst at a temperature of approximately 930° F. and under a superatmospheric pressure of about 100 pounds per square inch. The conversion products from both steps were supplied to the reaction chamber which was maintained at substantially the same pressure as that employed on the outlet of the catalytic reactor to which the light reflux condensate was supplied wherein said conversion products were subjected to substantial further cracking. The vaporous and liquid conversion products from the reaction chamber were sub-

stantially further vaporized in the vaporizing and separating chamber which was maintained under a superatmospheric pressure of approximately 50 pounds per square inch. The vaporous conversion products supplied to and evolved in the last mentioned chamber were separated therein from the non-vaporous residue which was recovered as a product of the process. The vaporous conversion products were subjected to fractionation, as previously described, under substantially the same pressure as that employed in the vaporizing and separating chamber. This operation will yield approximately 70% of 80 octane number gasoline by volume of the charge and 5% of non-vaporous residue, the balance being attributed normally to gas and loss. The gas produced contains a high proportion of readily polymerizable olefins, such as propene and butenes and is suitable stock for catalytic polymerization.

20 In a second operation a 25° A. P. I. gravity Mid-Continent topped crude was fractionated in commingled state with vaporous conversion products to separate fractionated vapors of the desired end boiling point from the higher boiling hydrocarbons. The fractionated vapors were condensed and recovered as a product of the process, while the higher boiling hydrocarbons were condensed in the fractionating zone as light and heavy reflux condensate. The light reflux condensate was contacted in essentially the vaporous state with a silica-alumina cracking catalyst at a temperature of approximately 930° F. and under a superatmospheric pressure of about 100 pounds per square inch. Simultaneously the heavy reflux condensate was contacted in essentially mixed phase with a silica-alumina cracking catalyst at a temperature of approximately 890° F. and under a superatmospheric pressure of about 400 pounds per square inch. The vaporous and liquid conversion products from both steps were supplied to the reaction chamber which was maintained at substantially the same pressure as that employed on the outlet of the catalytic reactor to which the light reflux condensate was supplied wherein said vaporous and liquid conversion products were subjected to substantial further cracking. The vaporous and liquid conversion products from the reaction chamber were substantially further vaporized in the vaporizing and separating chamber which was maintained under a superatmospheric pressure of approximately 50 pounds per square inch. The vaporous conversion products supplied to and evolved in the last mentioned chamber were separated therein from the non-vaporous residue which was recovered as a product of the process. The vaporous conversion products were subjected

to fractionation, as previously described, under substantially the same pressure as that employed in the vaporizing and separating chamber. The results of this operation were approximately 62% of 80 octane number gasoline by volume of the charge and 20% of non-vaporous residue, the balance being attributed normally to gas and loss.

I claim as my invention:

1. The process of catalytically cracking hydrocarbon oils, which comprises cracking a light reflux condensate, produced as hereinafter set forth, at a cracking temperature in contact with a cracking catalyst, simultaneously cracking a heavy reflux condensate, produced as hereinafter set forth, at a cracking temperature in contact with a cracking catalyst, commingling the resulting conversion products from both cracking operations and subjecting the mixture to non-catalytic conversion in a communicating reaction chamber by means of their contained heat, separating the resulting conversion products into vaporous and non-vaporous components and recovering the latter as a product of the process, fractionating said vaporous components in commingled state with hydrocarbon oil charging stock for the process to form said light and heavy reflux condensates which are supplied respectively to the two cracking steps, subjecting the resulting fractionated vapors to condensation, and recovering the resulting distillate.

2. A hydrocarbon oil conversion process which comprises simultaneously subjecting relatively light and heavy oils to independently controlled catalytic cracking in separate cracking zones, discharging resultant heated products from both said zones into a reaction zone and therein subjecting the same to non-catalytic cracking by the contained heat thereof, removing vapors from the reaction zone and subjecting the same to fractionation and condensation.

3. A hydrocarbon oil conversion process which comprises simultaneously subjecting relatively light and heavy oils to independently controlled catalytic cracking in separate cracking zones, discharging resultant heated products from both said zones into a reaction zone and therein subjecting the same to non-catalytic cracking by the contained heat thereof, removing vapors from the reaction zone, fractionating the same to form relatively light and heavy reflux condensates, supplying the relatively light and heavy reflux condensates respectively to the light oil cracking zone and the heavy oil cracking zone, and finally condensing the fractionated vapors.

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