

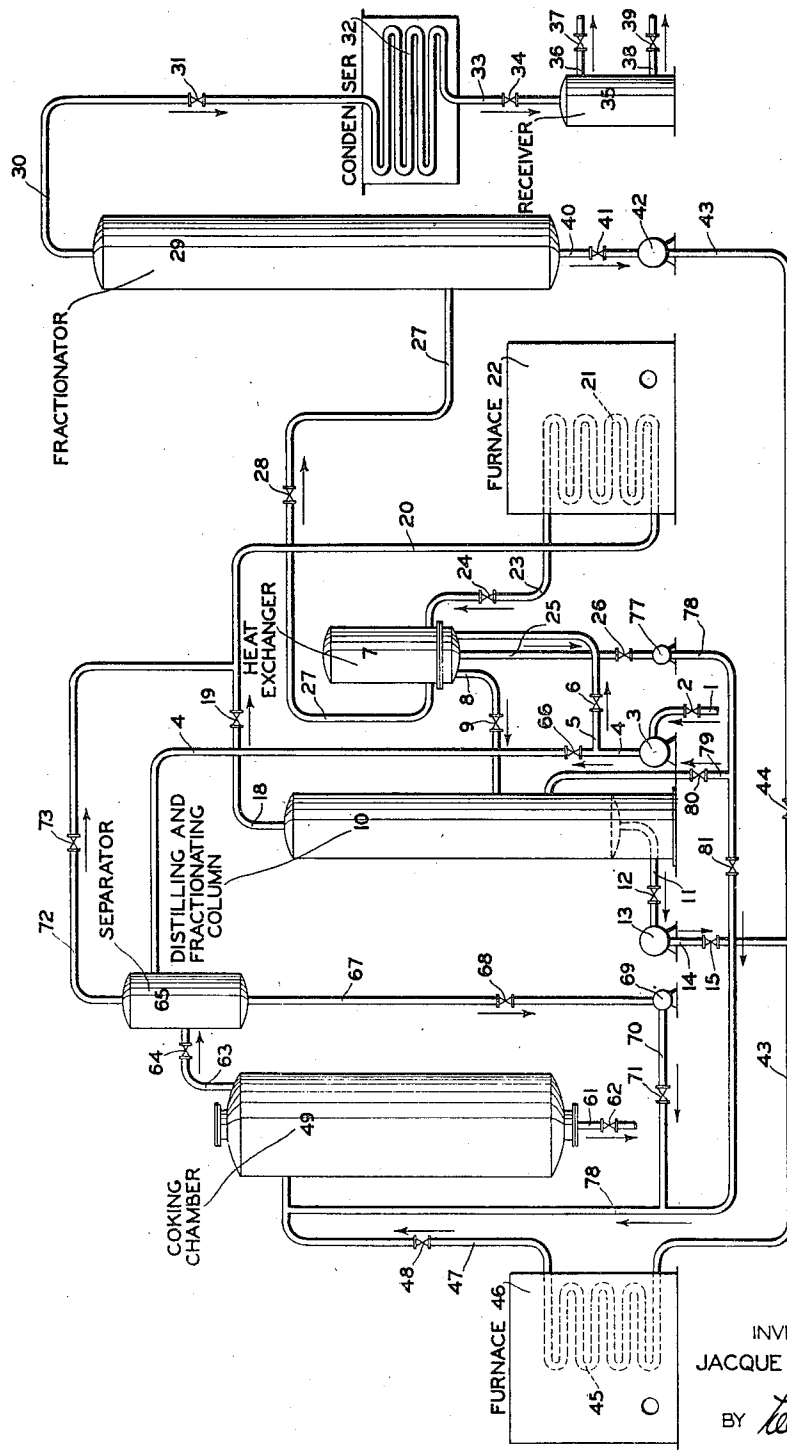
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CONVERSION OF HYDROCARBON OILS

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CONVERSION OF HYDROCARBON OILS

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This invention particularly refers to an improved process for the treatment of hydrocarbon oils of relatively wide boiling range embodying the cooperative steps of topping, cracking, coking and reforming.

In one embodiment, the present invention comprises subjecting charging stock for the process, comprising an oil of relatively wide boiling range, such as crude petroleum, for example, to fractional distillation whereby it is separated into relatively low-boiling and high-boiling fractions, subjecting said low-boiling fractions of the charging stock, including its components within the boiling range of motor fuel as well as, when desired, somewhat higher boiling fractions such as naphtha, kerosene or kerosene distillate and the like, to conversion or reforming in a heating coil, cooling the resulting products by indirect heat exchange with hydrocarbon oil charging stock for the process sufficiently to retard or arrest their further conversion, whereby the charging stock is heated sufficiently to effect or assist said fractional distillation thereof and whereby to remove heavy polymers and residual liquids from the vaporous conversion products, subjecting the vaporous conversion products to fractionation whereby their insufficiently converted components are condensed as reflux condensate, subjecting fractionated vapors of the desired end-boiling point to condensation, recovering and separating the resulting distillate and gas, subjecting said reflux condensate together with high-boiling fractions of the charging stock from said fractional distillation step to conversion conditions of elevated temperature and superatmospheric pressure in a separate heating coil, introducing the heated products into an enlarged coking chamber wherein the residual liquid conversion products are reduced to substantially dry coke, withdrawing vaporous products from the coking chamber, separating therefrom tars and similar high coke-forming materials, returning the latter to the coking chamber and subjecting the remaining vaporous products from the coking operation to further conversion in the first mentioned heating coil together with said low-boiling fractions of the charging stock.

It will be apparent from the foregoing as well as from the following further description of the process of the present invention that its various features and the various stages of the process are interdependent and mutually contribute to produce the desired final results.

The accompanying diagrammatic drawing il-

lustrates one specific form of apparatus in which the process of the invention may be accomplished.

Referring to the drawing, hydrocarbon oil charging stock preferably comprising, as already mentioned, an oil of relatively wide boiling range such as crude petroleum or the like, preferably containing a substantial proportion of both relatively low-boiling and relatively high-boiling fractions, is supplied through line 1 and valve 2 to pump 3 by means of which it is fed through lines 4 and 5 and valve 6 into heat exchanger 7, wherein it is subjected to indirect heat exchange with hot conversion products of the process and thereby heated to a temperature sufficient to effect its substantial vaporization and fractional distillation. The heated charging stock is discharged from the heat exchanger through line 8 and valve 9 into distilling and fractionating column 10. The charging stock may, of course, be subjected to heating in any well known manner, not illustrated, instead of or in conjunction with the heating accomplished in heat exchanger 7.

Distilling and fractionating column 10 may be operated at any desired pressure ranging from substantially atmospheric to a high superatmospheric pressure of the order of several hundred pounds per square inch and preferably a superatmospheric pressure is employed in this zone sufficient to permit the passage of the overhead vaporous products from column 10 to and through heating coil 21 without the aid of a vapor pump or compressor. The charging stock is separated by fractional distillation in column 10 into selected relatively low-boiling and high-boiling fractions. The latter are collected as bottoms in the lower portion of column 10 from which they are withdrawn through line 11 and valve 12 to pump 13, by means of which they are fed through line 14 and valve 15 and thence through line 43 to conversion in heating coil 45. The selective low-boiling fractions of the charging stock are withdrawn as fractionated vapors from the upper portion of column 10 through line 18 and valve 19 and are directed through line 20 to heating coil 21. It is, of course, within the scope of the invention, when desired, to employ a suitable vapor pump or compressor in line 18 in case heating coil 21 is operated at a higher pressure than that employed in column 10 or, when desired, the fractionated vapors may be subjected to condensation and the resulting distillate supplied by means of a suitable pump to heating coil 21, although these alternative meth-

ods of operation are not illustrated in the drawing. The invention also contemplates the separate recovery of any desired low-boiling, intermediate or high-boiling fraction of the charging stock, by well known means not illustrated, particularly when it contains valuable motor fuel fractions, lubricating stock, asphaltic material or the like.

Heating coil 21 is located within a furnace 22 of any suitable form by means of which the oil passing through the heating coil is subjected to the desired relatively high conversion temperature at any desired pressure. The hot conversion products are discharged from heating coil 21 through line 23 and valve 24 into heat exchanger 7 wherein they are cooled sufficiently, by indirect contact with charging stock for the process which is supplied to this zone as previously described, to prevent any appreciable further conversion thereof. Partial cooling of the conversion products in heat exchanger 7 also serves to remove therefrom by liquefaction undesirable heavy components such as heavy polymers, residual liquid and the like which may be withdrawn from the heat exchanger and directed through line 25 and valve 26 to pump 78, to be directed therefrom through line 78, line 79 and valve 80 into column 10, wherein they commingle with the high-boiling fractions of the charging stock and are directed therewith to further treatment as will be later more fully described. As an alternative method of operation the condensate from heat exchanger 7 may, when desired, be directed from pump 79 through line 78 and valve 81 to coking chamber 49. The vaporous products remaining uncondensed in heat exchanger 7 are directed therefrom through line 27 and valve 28 to fractionation in fractionator 29.

The components of the vaporous conversion products supplied to fractionator 29 boiling above the range of the desired final light distillate product of the process are condensed in this zone as reflux condensate, the reflux condensate is withdrawn from the lower portion of the fractionator through line 40 and valve 41 to pump 42 by means of which it is supplied through line 43 and valve 44 to conversion in heating coil 45, as will be later more fully described.

Fractionated vapors of the desired end-boiling point are withdrawn, together with uncondensable gas produced within the system, from the upper portion of fractionator 29 through line 30 and valve 31 and are subjected to condensation and cooling in condenser 32. The resulting distillate and gas passes through line 33 and valve 34 to collection and separation in receiver 35. Uncondensable gas may be released from the receiver through line 36 and valve 37. Distillate may be withdrawn from receiver 35 through line 38 and valve 39 to storage or to any desired further treatment. A regulated portion of the distillate collected in receiver 35 may, when desired, be recirculated by well known means, not shown in the drawing, to the upper portion of fractionator 29 to serve as a cooling and refluxing medium in this zone for assisting fractionation of the vapors and to maintain the desired vapor outlet temperature from the fractionator.

The oil supplied to heating coil 45, comprising reflux condensate from fractionator 29 and the high-boiling fractions of the charging stock from column 10, is subjected to the desired conversion temperature in the heating coil by means of heat supplied from a furnace 45, of any suitable form,

and the stream of hot conversion products is discharged from the heating coil through line 47 and valve 48 into coking chamber 49.

Coking chamber 49 may be operated at any desired pressure ranging from substantially atmospheric to several hundred pounds per square inch superatmospheric and preferably a superatmospheric pressure is employed in this zone sufficient to permit the passage of vaporous products therefrom through heating coil 21 without the use of a vapor pump or compressor. The liquid components of the conversion products supplied to the coking chamber are subjected to further distillation and/or conversion in this zone and the resulting residue is reduced to substantially dry coke. The coke may be allowed to accumulate within the coking chamber until it is substantially filled, following which the operation is discontinued and the chamber cleaned and prepared for further operation. When desired, a plurality of coking chambers may be employed, although only one is illustrated in the drawing, in which case they preferably are alternately operated, cleaned and prepared for further operation so that the duration of the operating cycle of the process is not limited by the capacity of the coking zone. Chamber 49 is provided with a suitable drain-line 61, controlled by valve 62, which may also serve as a means of introducing steam, water or any other suitable cooling medium into the chamber, after its operation is completed and after it has been isolated from the rest of the system, in order to hasten cooling and facilitate the removal of coke from the chamber.

It will be understood that, while coking of the residual liquid conversion products is particularly desirable in the operation of the present process, it may also be conducted, when desired, for the production of liquid residue. In such cases chamber 49 may function as a reaction and/or vaporizing chamber and the residual liquid product of the process may be withdrawn therefrom through line 61 and valve 62 to cooling and storage or elsewhere as desired.

Vaporous products are withdrawn from the upper portion of chamber 49 through line 63 and valve 64 to separator 65, wherein any heavy components and entrained liquid particles such as tars and similar heavy liquids of a high coke-forming nature are removed from the vapors. When desired, in order to assist the removal of said high boiling materials from the vaporous products from the coking zone, a regulated portion of the charging stock may be directed from pump 3 through valve 66 in line 4 into separator 65 and, when desired, regulated portions or selected fractions of the reflux condensate formed in fractionator 29, condensate from heat exchanger 7 or high boiling fraction of the charging stock from column 10 may be supplied, by well known means (not shown) to separator 65 for the same purpose. The high coke-forming liquids separated from the vaporous products from the coking chamber in separator 65 are withdrawn from the lower portion thereof through line 67 and valve 68 to pump 69 by means of which they are returned through line 70, valve 71 and line 78 to coking chamber 49 for further treatment and reduction to coke.

The vaporous products from the coking chamber escaping condensation in separator 65 are directed therefrom through line 72, valve 73 and line 20 to further conversion in heating coil 21, together with the low-boiling fractions of the

charging stock from column 10. It is, of course, within the scope of the invention, although not illustrated, to subject the vapors from separator 65 to condensation and to supply the resulting distillate by pump to conversion in heating coil 21, although this involves a considerable loss of heat by condensation of the vapors and is not the preferred method of operation.

The preferred range of operating conditions which may be employed in a process such as illustrated and above described may be approximately as follows: The heating coil to which the reflux condensate and the high-boiling fractions of the charging stock are supplied may employ a conversion temperature, measured at the outlet from the heating coil, ranging, for example, from 875 to 950° F., preferably with a superatmospheric pressure at this point in the system of from 100 to 500 pounds, or more, per square inch. The coking chamber may employ any desired pressure ranging from substantially the same as that employed at the outlet from the preceding heating coil down to substantially atmospheric pressure, although a superatmospheric pressure at least slightly above the pressure employed in the succeeding heating coil is preferred in the coking chamber. The distilling and fractionating column wherein the charging stock is subjected to fractional distillation may employ any desired pressure ranging from substantially atmospheric to 500 pounds, or more, per square inch, superatmospheric pressure and preferably a superatmospheric pressure slightly higher than that employed in the succeeding heating coil is utilized in the distilling and fractionating column. The heating coil to which the low-boiling fractions of the charging stock and the vaporous products from the coking chamber are supplied may utilize an outlet conversion temperature ranging, for example, from 950 to 1100° F. with a pressure which may range, for example, from substantially atmospheric to 500 pounds, or more, per square inch, the higher temperatures normally being employed when lower pressures are utilized. The fractionating, condensing and collecting portions of the system may employ pressures substantially the same or lower than the pressure employed at the outlet from the last mentioned heating coil.

As a specific example of the operation of the process of the present invention as it may be accomplished in an apparatus such as illustrated and above described, the charging stock comprises a California crude of about 33° A. P. I. gravity containing approximately 36 per cent of material boiling up to 437° F. and it is subjected to fractional distillation by means of heat supplied thereto by indirect heat exchange with the hot conversion products from the heating coil to which the low-boiling fractions of the charging stock are supplied. The charging stock is separated by said fractional distillation into fractions boiling above and below approximately 600° F. The high-boiling fractions of the charging stock are subjected, together with reflux condensate from the fractionator of the cracking system, to a conversion temperature, measured at the outlet from the heating coil to which they are supplied, of approximately 950° F. at a superatmospheric pressure of approximately 175 pounds per square inch, which pressure is substantially equalized in the succeeding coking chamber. Heavy materials of a high coke-forming nature, such as entrained tars and residual oils, are separated from the vaporous products

removed from the coking chamber and are returned to the coking chamber for further treatment and reduction to coke, the remaining vaporous products from the coking chamber are supplied, together with the low-boiling fractions of the charging stock, to a separate heating coil wherein they are subjected to a conversion temperature, measured at the outlet therefrom, of approximately 1000° F. at a superatmospheric pressure, also measured at the outlet from the heating coil, of approximately 60 pounds per square inch. The stream of highly heated products from the last mentioned heating coil are cooled by indirect heat exchange with the charging stock sufficiently to prevent any appreciable further conversion thereof and the cooling also serves to separate from the vaporous conversion products high-boiling liquids, such as polymers and residual oils, which are returned to the coking chamber. The remaining vaporous products are subjected to fractionation for the formation of said reflux condensate and the fractionated vapors are subjected to condensation for recovery of the final light distillate product of the process and gas. This operation may produce, per barrel of charging stock, approximately 60 per cent of 400° F. end-point motor fuel having an octane member of approximately 72, the additional products of the process being approximately 60 pounds of petroleum coke suitable as fuel and the remainder uncondensable gas.

I claim as my invention:

1. A process which comprises topping crude petroleum containing straight run gasoline to separate therefrom a light fraction containing gasoline boiling hydrocarbons, distilling the topped crude to coke, separating high-boiling components from the overhead products of the coking operation, combining the lighter components of said overhead products with said light fraction of the crude, passing the resultant mixture through a heating coil and subjecting the same therein to cracking conditions of temperature and pressure adequate to increase the anti-knock value of the gasoline hydrocarbons contained therein, cooling the resultant conversion products, promptly upon discharge from said coil, by indirect heat exchange with crude oil being supplied to the topping operation whereby to preheat the crude and separate heavy constituents of the conversion products, supplying such separated heavy constituents to the coking operation, and fractionating and condensing the cooled conversion products uncondensed by said heat exchange.

2. A combined topping, cracking and reforming process which comprises partially vaporizing crude petroleum without substantial cracking thereof and separating therefrom a vapor containing straight run gasoline, subjecting portions of the crude heavier than gasoline to cracking conditions of temperature and pressure in a heating coil and separating the resultant products into vapors and residue in an enlarged chamber, cooling the last-named vapors to separate heavy fractions thereof while retaining the gasoline formed by the cracking in vapor state, combining the vapors uncondensed by said cooling with said vapor containing straight run gasoline, subjecting the resultant vaporous mixture in a second heating coil, maintained at higher temperature than the first-named coil, to conversion conditions adequate to increase the anti-knock value of gasoline fractions contained therein,

cooling the vaporous conversion products thus formed by indirect heat exchange with crude petroleum being supplied to the partial vaporizing step and thereafter fractionating the uncondensed portion thereof independently of the crude petroleum and of the vapors separated in said chamber to condense fractions thereof heavier than gasoline, supplying reflux condensate formed by the fractionation to the first-named coil for cracking treatment therein, and finally condensing and collecting the fractionated vapors.

3. A combined topping, cracking and reforming process which comprises partially vaporizing crude petroleum without substantial cracking thereof and separating therefrom a vapor containing straight run gasoline, cracking portions of the crude heavier than gasoline to produce gasoline therefrom, cooling the resultant cracked vapors to separate heavy fractions thereof while retaining the gasoline formed by the cracking

in vapor state, combining the vapors uncondensed by said cooling with said vapor containing straight run gasoline, subjecting the resultant vaporous mixture, independently of said heavier portions of the crude, to reforming to increase the anti-knock value of gasoline fractions contained therein, cooling the vaporous conversion products thus formed by indirect heat exchange with crude petroleum being supplied to the partial vaporizing step and thereafter fractionating the uncondensed portion thereof independently of the crude petroleum and of said cracked vapors to condense fractions thereof heavier than gasoline, supplying reflux condensate formed by the fractionation to the cracking step for treatment therein together with said heavier portions of the crude, and finally condensing and collecting the fractionated vapors.

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