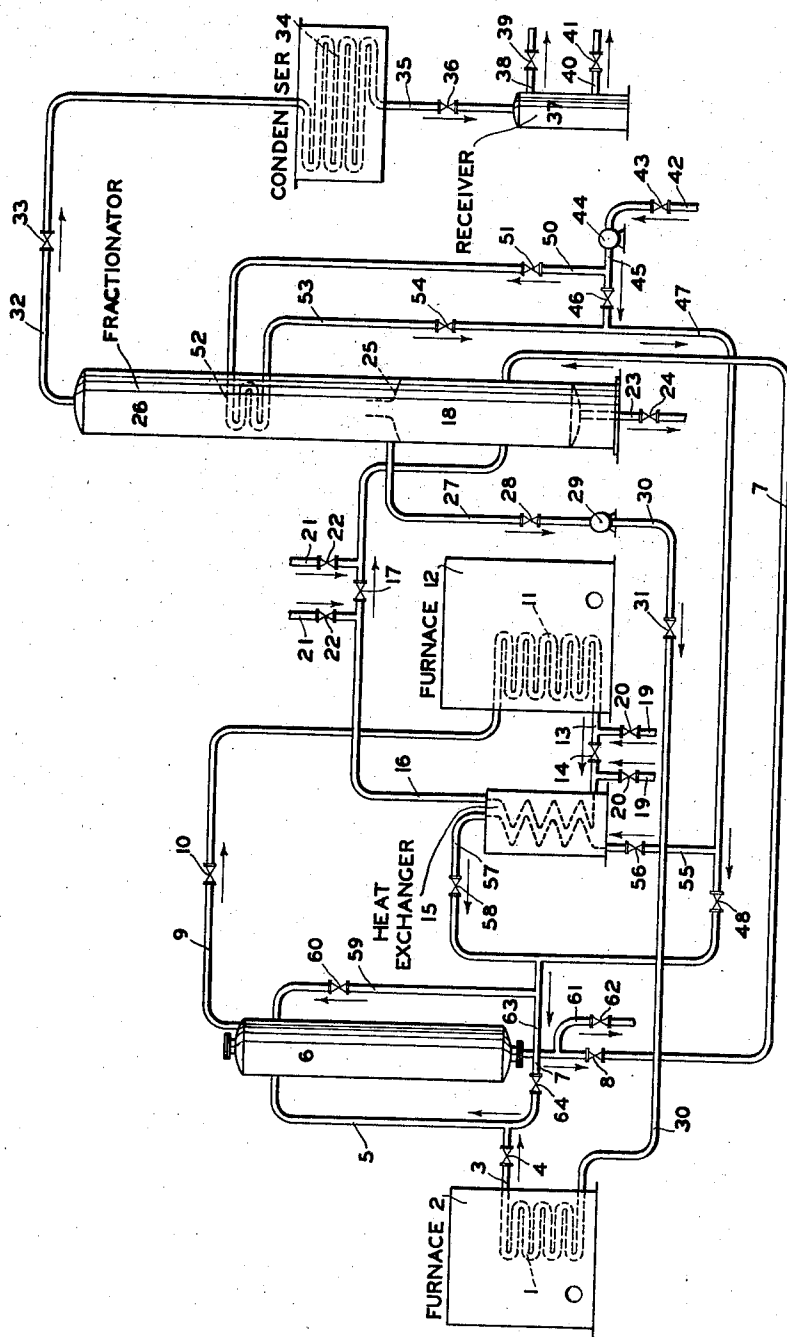


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CONVERSION OF HYDROCARBON OILS
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CONVERSION OF HYDROCARBON OILS

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2 Claims. (Cl. 196—60)

This is a continuation-in-part of my co-pending application Serial No. 2,581 which was filed on January 19, 1935.

The invention particularly refers to an improved process for the simultaneous pyrolytic conversion of relatively low-boiling and relatively high-boiling hydrocarbon oils, each under independently controlled cracking conditions.

In this process intermediate liquid conversion products, formed as later described, are cracked at elevated temperature and superatmospheric pressure, the resulting heated products commingled with hydrocarbon oil charging stock for the process, the commingled materials subjected to continued relatively mild cracking in an enlarged reaction chamber also preferably maintained at a substantial superatmospheric pressure, resultant vaporous and liquid products separated in said reaction chamber, the vapors further cracked in a separate independently controlled cracking zone, the vaporous components of the conversion products resulting from the last mentioned cracking operation fractionated to form said intermediate liquid products, which are supplied to the first mentioned cracking operation, and fractionated vapors of the desired end-boiling point condensed to form a distillate which is recovered as the final gasoline produce of the process.

The invention is particularly advantageous as applied to the treatment of relatively heavy charging stocks, since in the present process such materials may be cracked in the reaction chamber, thus avoiding the necessity of passing the same through a cracking coil and thereby obviating the difficulties, such as coke deposition and excessive gas production, normally encountered in cracking coils devoted to the treatment of readily decomposed high-boiling oils.

The invention is also advantageous as applied to the treatment of charging stocks consisting of or containing appreciable quantities of relatively low-boiling materials such as poor antiknock gasoline or gasoline fractions, naphtha, kerosene distillate and the like. With this type of charging stock the same is substantially vaporized in the reaction chamber and its low-boiling vaporous components, together with the vaporous products of the first mentioned cracking operation, are cracked in said separate cracking zone to produce high yields of good antiknock gasoline.

As applied to the treatment of wide boiling range charging stock, its low-boiling components are vaporized in the reaction chamber and subse-

quently cracked in said separate cracking zone with the vaporous components of the conversion products of the first mentioned cracking operation, while its high-boiling components are more mildly cracked within the reaction chamber.

The invention provides various methods of preheating the charging stock, prior to its introduction into the reaction chamber, by direct and/or indirect heat exchange with relatively hot vaporous products of the process. In addition to preheating the charging stock, the various heat exchange steps provided serve other useful and advantageous purposes which will be later described. The invention also provides for partially cooling various relatively hot conversion products at selected intermediate points in the system either for the purpose of retarding or preventing further cracking of said heated products and/or for the purpose of assisting separation of the heated products into the desired vaporous and liquid components. It should, however, be understood that the invention in its broadest sense is not limited to the specific manner in which the preheating and partial cooling steps hereinafter illustrated and described are accomplished.

One specific embodiment of the invention comprises preheating hydrocarbon oil charging stock for the process to a temperature below that at which any substantial cracking thereof will occur, commingling the preheated charging stock in a reaction chamber with relatively hot conversion products, formed as later described, thereby partially cooling said hot conversion products and further heating the charging stock to a relatively mild cracking temperature, cracking the commingled materials at said relatively mild temperature and at substantial superatmospheric pressure in said reaction chamber, separately removing the resulting vaporous and liquid conversion products from the reaction chamber, supplying the vapors to a vapor cracking coil, therein heating the same to a high cracking temperature, discharging the resulting highly heated products from said cracking coil, cooling the same sufficiently to prevent any excessive further cracking thereof, separating the partially cooled products into vaporous and residual liquid components, fractionating said vaporous components to form reflux condensate, supplying the latter to a separate cracking coil, therein heating the same to a high cracking temperature at substantial superatmospheric pressure, commingling the resulting highly heated products with the preheated charging stock as aforementioned, subjecting vaporous products of the desired end-boiling point from

said fractionating step to condensation and recovering the resulting distillate.

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

Referring to the drawing, reflux condensate formed within the system and supplied, as will be later described, to heating coil 1 is heated therein to the desired cracking temperature at superatmospheric pressure by means of heat supplied from furnace 2. The resulting products are discharged from coil 1 through line 3 and valve 4 and are directed through line 5 into reaction chamber 6.

The charging stock for the process is simultaneously supplied to chamber 6, as will be later described, and the commingled charging stock and conversion products from coil 1 are mildly cracked in chamber 6 at a lower temperature than that maintained at the outlet of heating coil 1. A substantial superatmospheric pressure is also preferably maintained in chamber 6 and may be somewhat lower or substantially the same as that employed at the outlet of coil 1. Vaporous and liquid components of the materials supplied to and/or formed within chamber 6 are separated in this zone. The residual liquid is removed from the lower portion of chamber 6 through line 7 and may pass, all or in part, through line 61 and valve 62 to cooling and storage or to any desired further treatment, or it may be directed, all or in part, through valve 8 in line 7 to flash distillation in chamber 18. The vaporous products are directed from the upper portion of chamber 6 through line 9 and valve 10 to further treatment in heating coil 11.

Coil 11 is disposed within and supplied with heat from furnace 12, by means of which the vaporous products passing through this zone are heated to a relatively high cracking temperature at substantially the same or at lower pressure than that maintained in chamber 6. The resulting hot conversion products are discharged from coil 11 through line 13 and may be directed through valve 14 in this line to and through heat exchanger 15, wherein they are partially cooled by indirect heat exchange with charging stock for the process. The conversion products from heating coil 11 are thence directed from heat exchanger 15 through line 16 and valve 17 into separating chamber 18.

Means are provided in the case here illustrated for additional cooling of the heated products discharged from coil 11 whereby to reduce their temperature sufficiently to prevent any substantial further cracking thereof. This additional cooling, when required, is accomplished by introducing a suitable cooling oil into line 13 through one or more lines 19 controlled by valves 20, on either or both sides of valve 14, prior to said indirect heat exchange between the charging stock and the conversion products, or cooling oil may be introduced into line 16 through one or more lines 21 controlled by valves 22, on either or both sides of valve 17, following said indirect heat exchange between the charging stock and the conversion products. The material employed as cooling oil in line 13 and/or 16 may comprise, for example, regulated quantities of the final light distillate products of the process and/or regulated quantities or selected fractions of intermediate liquid conversion products of the process such as, for example, reflux condensate from fractionator 26. Such materials may be

pumped from their sources through lines 19 and/or 21 by well known means not shown.

The partially cooled conversion products supplied, as above described, to chamber 18 are separated in this zone into vaporous and residual liquid fractions, the latter being removed from the lower portion of this zone through line 23 and valve 24 to cooling and storage or to any desired further treatment, while the vaporous products are directed from the upper portion of chamber 18 through a suitable partition or the like 25 into fractionator 26.

Fractionator 26, in the particular case here illustrated, comprises the upper portion of the same column which houses separating zone 18. Separate structures may, of course, be employed for chamber 18 and fractionator 26, when desired.

High-boiling components of the products supplied to fractionator 26 are condensed within this zone as reflux condensate. The latter is withdrawn from the lower portion of fractionator 26 and directed through line 27 and valve 28 to pump 29 by means of which it is supplied through line 30 and valve 31 to conversion, as previously described, in heating coil 1.

Fractionated vapors of the desired end-boiling point are removed from the upper portion of fractionator 26 and directed through line 32 and valve 33 to cooling and condensation in condenser 34. The resulting distillate and uncondensed normally gaseous products pass from condenser 34 through line 35 and valve 36 to collection and separation in receiver 37. The uncondensed gases may be released from the receiver through line 38 and valve 39. The distillate product, which preferably comprises gasoline of good anti-knock value, is removed from receiver 37 through line 40 and valve 41 to storage or to any desired further treatment.

When desired, regulated quantities of the distillate collected in receiver 37 may be recirculated, by well known means, not illustrated, to the upper portion of fractionator 26 to serve as a cooling and refluxing medium in this zone.

Hydrocarbon oil charging stock for the process is supplied through line 42 and valve 43 to pump 44 wherefrom it may be fed, all or in part, through line 45, valve 46, line 47, valve 48 and line 63 and valve 64 into line 5, commingling therein with the heated products discharged from heating coil 1 and passing therewith into reaction chamber 6. Preferably, however, the charging stock is preheated to a temperature below that at which any substantial cracking thereof will occur prior to commingling with the heated products from heating coil 1. To accomplish this, provision is made, in the case here illustrated, for passing all or any desired portion of the charging stock in indirect heat exchange with the vaporous products undergoing fractionation in fractionator 26, this being accomplished by diverting charging stock from line 45 through line 50 and valve 51 into and through closed coil 52 disposed within fractionator 26, wherefrom the charging stock, after being preheated by indirect heat exchange with the vaporous products undergoing fractionation, is directed through line 53 and valve 54 into line 47. Provision is also made, as previously indicated, for passing a regulated portion or all of the charging stock in indirect heat exchange with heated products discharged from coil 11. This is accomplished by diverting regulated quantities of the charging stock from line 47 through line 55 and valve 56 into and through heat exchanger 15, where-

from it is directed through line 57 and valve 58 into line 63.

When desired, instead of commingling the charging stock in line 5 with the stream of highly heated products discharged from heating coil 1, the preheated charging stock may be introduced directly into chamber 6 at any desired point or plurality of points in this zone and, as an illustration of the means whereby this may be accomplished, line 59 and valve 60 are provided in the case here illustrated.

It will, of course, be understood that the invention is not limited to the specific form of apparatus illustrated and above described, since other forms of apparatus may be utilized to accomplish substantially the same results.

The preferred range of operating conditions which may be employed, in an apparatus such as illustrated and above described, for conducting the process of the invention may be approximately as follows: The temperature employed at the outlet of heating coil 1 may range, for example, from 875 to 950° F., or more, preferably with a superatmospheric pressure at this point in the system of from 150 to 500 pounds, or more, per square inch. As previously mentioned, the superatmospheric pressure employed in chamber 6 may be substantially the same or lower than that utilized at the outlet of heating coil 1. Preferably, the charging stock is heated to a temperature of the order of 600 to 800° F., or thereabouts, prior to its introduction into chamber 6 and the temperature employed in the latter zone is preferably of the order of 850 to 900° F., or more. The temperature employed at the outlet of heating coil 11 may range, for example, from 950 to 1150° F., or thereabouts, and preferably this zone is operated at a substantial superatmospheric pressure which may be substantially the same or somewhat lower than that employed in chamber 6. However, when desired, reduced pressures down to 30 pounds, or thereabouts, per square inch, superatmospheric, may be employed at the outlet of heating coil 11. Preferably, the products discharged from coil 11 are cooled to a temperature of the order of 600 to 800° F., prior to their introduction into chamber 18. Chamber 18 and the succeeding fractionating, condensing and collecting portions of the system may utilize pressures substantially the same or lower than that employed at the outlet of heating coil 11.

As a specific example of an operation of the process, as it may be conducted in an apparatus such as illustrated and above described, the charging stock is an uncracked Mid-Continent residue of approximately 18° A. P. I. gravity and is heated, first by indirect heat exchange with the products undergoing fractionation and then by indirect heat exchange with the products discharged from the vapor heating coil of the system, to a temperature of approximately 730° F. Reflux condensate formed in fractionator 26 is heated in coil 1 to an outlet conversion temperature of approximately 950° F., the resulting highly heated products commingled with the preheated charging stock and the commingled materials subjected to cracking in reaction chamber 6. The pressure employed at the outlet of heating coil 1 is approximately 350 pounds per square inch and substantially the same pressure is employed in the reaction chamber. The average temperature in the latter zone is approximately 850° F. Residual liquid is removed from the reaction chamber and the vaporous products from

this zone are cracked in heating coil 11. The temperature employed at the outlet of heating coil 11 is approximately 1000° F. and the pressure at the inlet of coil 11 is substantially the same as that employed in the reaction chamber, vaporous products from the latter zone being supplied to coil 11 without the use of a pump or compressor. A somewhat lower pressure prevails at the outlet of coil 11, due to friction through the coil. Regulated quantities of the reflux condensate formed in fractionator 26 are utilized as a direct cooling medium for the products discharged from coil 11, whereby the latter are cooled to a temperature of approximately 650° F. prior to their introduction into chamber 18. Residual liquid from reaction chamber 6 is supplied to chamber 18 wherein it is flash distilled, chamber 18 being operated at a superatmospheric pressure of approximately 75 pounds per square inch. Substantially the same pressure is employed in fractionator 26 and vaporous products from this zone are condensed to form the final gasoline product of the process which has an end-boiling point of approximately 400° F. This operation will produce, per barrel of charging stock, approximately 55% of 400° F. end-point gasoline having an octane number of approximately 70, as determined by the motor method, and about 33% of flashed residue which is suitable as fuel oil, the remainder being chargeable to normally gaseous products and loss.

I claim as my invention:

1. In a process for the pyrolytic conversion of hydrocarbon oils wherein reflux condensate, formed within the system as hereinafter described, is heated to cracking temperature at superatmospheric pressure, the resulting heated products commingled with hydrocarbon oil charging stock for the process, the commingled materials appreciably cracked at the attained temperature of the mixture and at substantial superatmospheric pressure in an enlarged reaction zone and the resultant vapors and liquid conversion products separately removed from said enlarged reaction zone, the improvement which comprises supplying residual liquid removed from said reaction zone to a zone of substantially reduced pressure and therein flash distilling the same, separately heating said vapors removed from the reaction zone to a high cracking temperature, cooling the resulting hot conversion products to a sufficiently low temperature to prevent any excessive continued cracking thereof, introducing the cooled products into said zone of substantially reduced pressure, separating vapors and non-vaporous residue in said zone of substantially reduced pressure, fractionating the last named vapors to form said reflux condensate, which is returned to the first mentioned cracking operation, condensing fractionated vapors of the desired end-boiling point, recovering the resulting distillate and preheating said charging stock to a temperature below that at which any substantial cracking thereof will occur prior to commingling the same with the heated products of the first mentioned cracking operation, said preheating including the step of passing regulated quantities of said charging stock in indirect heat exchange with relatively hot products of the cracking step to which said vapors from the reaction zone are supplied, whereby to accomplish at least a portion of said cooling of the hot conversion products.

2. A process for the pyrolytic conversion of

hydrocarbon oils, which comprises heating reflux condensate, formed within the system as hereinafter described, to cracking temperature at superatmospheric pressure in a heating coil, discharging the resulting products into an enlarged reaction chamber and commingling the same with hydrocarbon oil charging stock for the process which has been preheated, as hereinafter described, to a temperature below that at which any substantial cracking of the charging stock will occur, cracking the commingled materials at the attained temperature of the mixture and at superatmospheric pressure in said reaction chamber, separately removing resultant vapors and liquid conversion products from the reaction chamber, supplying liquid products removed from said reaction chamber to a zone of substantially reduced pressure and therein flash distilling the same, passing said vapors removed from the reaction chamber, by means of the superatmospheric pressure maintained therein,

through a separate heating coil and therein heating the same to a higher cracking temperature than that employed in the first mentioned heating coil, cooling the highly heated products of the last mentioned cracking operation to a sufficiently low temperature to prevent any excessive continued cracking thereof, said cooling step comprising indirect heat exchange between regulated quantities of the charging stock and relatively hot products of the vapor-cracking step, whereby to supply at least a portion of said preheat to the charging stock, introducing the partially cooled products of said vapor-cracking step into said zone of substantially reduced pressure, therein separating vapors and non-vaporous residue, fractionating the last named vapors to form said reflux condensate, which is supplied to the first mentioned heating coil, condensing fractionated vapors of the desired end-boiling point, and recovering the resulting distillate.

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