

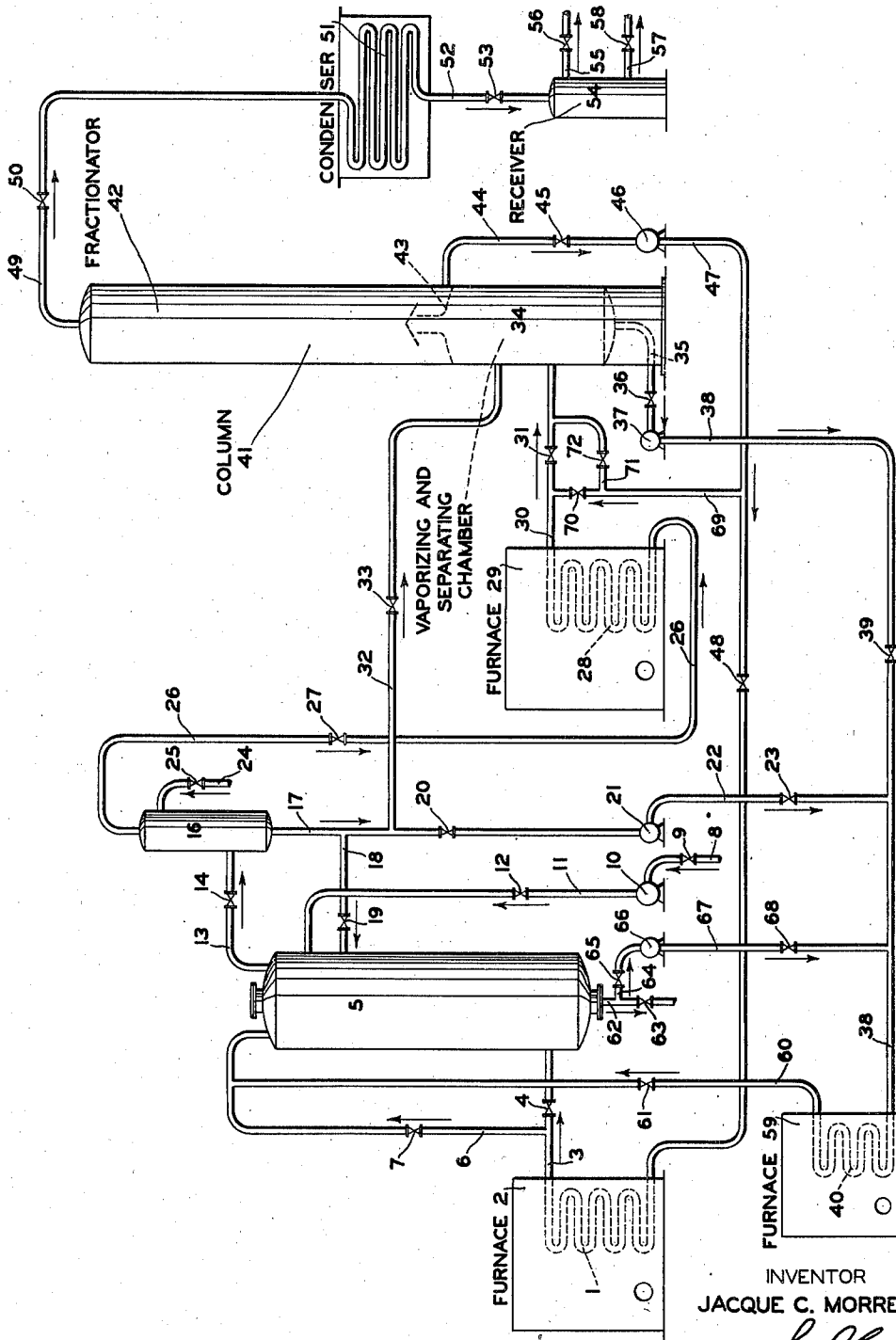
Aug. 9, 1938.

J. C. MORRELL

2,126,204

CONVERSION OF HYDROCARBON OILS

Filed Sept. 28, 1935



INVENTOR
JACQUE C. MORRELL
BY *J. C. Gary*
ATTORNEY

UNITED STATES PATENT OFFICE

2,126,204

CONVERSION OF HYDROCARBON OILS

Jacque C. Morrell, Chicago, Ill., assignor to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

Application September 28, 1935, Serial No. 42,699

11 Claims. (Cl. 196—60)

This invention particularly refers to an improved process for the pyrolytic conversion of hydrocarbon oils wherein intermediate liquid conversion products of the process are subjected to conversion conditions of cracking temperature and superatmospheric pressure, and thence commingled with the relatively cool hydrocarbon oil charging stock for the process in a zone wherein vaporous and liquid products are separated, the vaporous products subjected to continued conversion in a separate heating coil, the resulting vaporous conversion products subjected to fractionation for the formation of said intermediate liquid conversion products and the recovery of desirable light distillate, while residual liquid products resulting from one or both of the cracking stages are subjected to further heating under cracking conditions, either for the purpose of substantially reducing their viscosity or for effecting their subsequent reduction to coke, the resulting heated products being introduced into the same chamber to which the charging stock and the hot conversion products from the first-mentioned cracking stage are supplied.

In one specific embodiment, the invention comprises subjecting intermediate liquid conversion products recovered from within the system, as will be later described, to conversion conditions of cracking temperature and substantial superatmospheric pressure in a heating coil, introducing the resulting heated products into an enlarged coking chamber to which hydrocarbon oil charging stock for the process is supplied, whereby the charging stock is heated and subjected to substantial vaporization and whereby vaporous and non-vaporous components of the commingled charging stock and conversion products are separated, said non-vaporous components being reduced therein to coke, withdrawing the commingled vapors from the coking chamber, separating therefrom undesirable components including entrained tars and pitch-like materials, returning the latter to further treatment within the same system, subjecting the remaining vaporous products to additional conversion under independently controlled heating conditions in a separate heating coil, separating the vaporous and liquid conversion products resulting from the last-mentioned cracking stage, subjecting said vaporous products to fractionation for the formation of reflux condensate, comprising said intermediate liquid conversion products which are supplied to the first-mentioned heating coil, subjecting fractionated vapors of the desired end-boiling point to condensation, recovering the re-

sulting distillate, subjecting said liquid conversion products from the last-mentioned separating stage to additional heating under non-coking conditions in another separate heating coil, and introducing the resulting heated products into said coking chamber wherein they are reduced to coke.

Various alternatives and modifications to the process above outlined may be employed without departing from the scope of the invention. For example, a reaction or vaporizing chamber may be substituted for the coking zone and operated under conditions favorable to the production of good quality liquid residue instead of coke, in which case the conversion conditions under which the liquid products from said last-mentioned separating stage are subjected to additional heating are regulated to effect a material reduction of their viscosity without effecting their excessive conversion and coking. In such cases, it is also within the scope of the invention, when desired, to return regulated quantities of the residual liquid product recovered from the reaction or vaporizing chamber to the heating coil wherein said viscosity breaking operation is accomplished.

The various embodiments of the process above outlined, as well as other modifications and alternatives which are within the scope of the invention, are illustrated in the accompanying diagrammatic drawing, the following description of which will serve to more clearly illustrate the various flows and conditions of operation required to accomplish the various objects of the invention.

Referring to the drawing, heating coil 1 is located within a furnace 2, by means of which the intermediate liquid conversion products of the process supplied to this zone in the manner to be later described are subjected to the desired cracking temperature, preferably at a substantial superatmospheric pressure. The heated products are discharged in a continuous stream from the heating coil through line 3 and may be directed, all or in part, through valve 4 in this line into the lower portion of chamber 5 or through line 6 and valve 7 into the upper portion of chamber 5, or they may be supplied, all or in part, to any other desired point or plurality of points in the chamber not illustrated.

Chamber 5, depending primarily upon the type of oil undergoing treatment and the desired products, may be operated either for the production of liquid residue or relatively dry coke from the relatively high-boiling liquids supplied to this zone, and, depending upon the type of operation

employed and the desired results, may be operated at any desired pressure ranging from substantially atmospheric up to a superatmospheric pressure substantially the same as that employed at the outlet from heating coil 1.

Simultaneously with the operation described, charging stock for the process, which may comprise any desired type of hydrocarbon oil ranging from motor fuel or naphtha through the various grades and fractions of crude petroleum as well as cracked hydrocarbons to heavy residual oil and specifically including crudes or other oils of relatively wide boiling range, is supplied through line 8 and valve 9 to pump 10 by means of which it is introduced in relatively cool state through line 11 and valve 12 into chamber 5. The charging stock is commingled in chamber 5 with the hot conversion products supplied to this zone and is thereby subjected to substantial vaporization, its high-boiling components commingling with the residual conversion products in this zone while its low-boiling vaporous components are directed together with the vaporous conversion products from the upper portion of chamber 5 through line 13 and valve 14 to separating chamber 16, which may be of any desired form and is provided for the purpose of removing from the vapors any undesirable high-boiling components including entrained tars, pitches and other heavy oils of high coke-forming characteristics.

The heavy liquid products removed from the vapors in chamber 16 are withdrawn from the lower portion of this zone through line 17 and may be returned by gravity or by means of a suitable pump, not shown, through line 18 and valve 19 to further treatment in chamber 5, or they may be directed through valve 20 in line 17 to pump 21 by means of which they are fed through line 22, valve 23 and line 33 to further treatment in heating coil 40, the function of which will be later described. In case chamber 5 and separating chamber 16 are operated at substantial superatmospheric pressure, it is also within the scope of the invention, when desired, to supply the high-boiling liquids removed from chamber 16 through line 32 and valve 33 into reduced pressure vaporizing chamber 34 wherein they are subjected to further vaporization and wherefrom the remaining non-vaporous components are supplied to further treatment in heating coil 40, as will be later more fully described. It is also within the scope of the invention to supply any suitable cooling medium to chamber 16, passing the same in either direct or indirect heat exchange with the materials supplied to this zone from chamber 5, and, when desired, fractionating means of any suitable form, not illustrated, such as baffles, perforated pans, bubble trays and the like may be employed in chamber 16 for assisting the separation of heavy liquid components from the vaporous products. Line 24 controlled by valve 25 illustrates means which may be employed for introducing cooling material into this zone, which may comprise, for example, regulated quantities of the total or selected fractions of the intermediate liquid conversion products of the process, regulated quantities of the charging stock or suitable oil from an external source which may, when desired, be of such a nature and be employed in such quantities as to function as a separate charging stock.

The vaporous products remaining uncondensed in chamber 16 are directed therefrom through line 26 and valve 27 to conversion in heating coil

28. Heating coil 28 is supplied with the heat from a furnace 29 to subject the oil passing through the heating coil to the desired conversion temperature under the desired pressure conditions which may range from substantially atmospheric pressure to a super-atmospheric pressure of several hundred pounds per square inch. Preferably, when a substantial superatmospheric pressure is employed in chamber 5, substantially the same or a somewhat lower superatmospheric pressure is employed in heating coil 28. On the other hand, when substantially atmospheric or a relatively low superatmospheric pressure is employed in chamber 5, conditions within the range of what is commonly termed "vapor-phase cracking" employing substantially atmospheric or relatively low superatmospheric pressure are preferred in heating coil 28, although it is entirely within the scope of the invention, when desired, to employ a suitable pump or compressor in line 26 in order that the pressure employed in chamber 5 may be materially increased in heating coil 28. The conversion products are discharged from heating coil 28 through line 30 and valve 31 into vaporizing chamber 34, preferably being cooled within this zone or prior to their introduction thereto to a sufficiently low temperature to prevent any substantial continued conversion thereof. This may be accomplished, for example, by indirect heat exchange with the charging stock or with any desired relatively cool vaporous or liquid product of the process by well known means, not illustrated, or by commingling the stream of hot conversion products, as will be later more fully described, with a suitable cooling oil, preferably recovered from within the system.

Chamber 34 is preferably operated at substantially atmospheric or a relatively low superatmospheric pressure, and in case a substantial superatmospheric pressure is employed in heating coil 28, the pressure reduction in chamber 34 serves to assist cooling of the stream of hot conversion products from the heating coil and to assist vaporization of their high-boiling components. Separation of vaporous and residual liquid conversion products is accomplished in chamber 30, the latter being withdrawn from the lower portion of this zone through line 35 and valve 36 to pump 37 by means of which they are supplied through line 38 and valve 39 to further treatment in heating coil 40, in the manner to be subsequently described.

In the particular case here illustrated, vaporizing and separating chamber 34 comprises the lower portion of column 41, the upper portion of which comprises fractionator 42 although separate structures may be employed for these two zones, when desired. Vaporous products from chamber 34 pass through a suitable partition into fractionator 42 wherein their components boiling above the range of the desired final light distillate product of the process are condensed as reflux condensate. The reflux condensate is withdrawn from the lower portion of the fractionator through line 44 and valve 45 to pump 46 by means of which it is supplied through line 47 and valve 48 to conversion, as previously described, in heating coil 1.

Fractionated vapors of the desired end-boiling point are withdrawn together with uncondensable gas produced by the operation from the upper portion of fractionator 42 and are directed through line 49 and valve 50 to condensation and cooling in condenser 51. The resulting dis-

tillate and gas pass through line 52 and valve 53 to collection and separation in receiver 54. Uncondensable gas may be released from the receiver through line 55 and valve 56. Distillate may be withdrawn from receiver 54 through line 57 and valve 58 to storage or to any desired further treatment. When desired, regulated quantities of the distillate collected in receiver 54 may be recirculated by well known means, not illustrated in the drawing, into the upper portion of fractionator 42 to serve as a refluxing and cooling medium in this zone for assisting fractionation of the vapors and to maintain the desired vapor outlet temperature therefrom.

Heating coil 40 is located within a furnace 59, by means of which the oil passing through the heating coil is subjected to the desired temperature and pressure conditions. The conditions employed in heating coil 40 will depend, primarily, upon whether the process is operated for the production of liquid residue or coke in chamber 5. In case it is desired to produce substantially dry coke as the final residual product of the process, the residual liquid from chamber 34, as well as, when desired, the high-boiling liquids removed from the vaporous products in chamber 16, are quickly heated to a relatively high conversion temperature in heating coil 40 without allowing them to remain in this zone for a sufficient length of time to permit any substantial formation or deposition of coke in this zone or in the communicating lines. In case it is desired to produce good quality liquid residue in chamber 5 as the final residual product of the process, milder conversion temperatures within the range of what are now commonly known as viscosity-breaking conditions are employed in heating coil 40. In case the latter method of operation is employed, it is within the scope of the invention, when desired, to supply regulated quantities of the residual liquid withdrawn through line 62 from the lower portion of chamber 5 through line 64 and valve 65 to pump 66 by means of which they are directed through line 67, valve 68 and line 38 to further conversion or viscosity breaking in heating coil 40. The heated products are discharged from heating coil 40 through line 60 and may be introduced through valve 61 in this line into the upper portion of chamber 5 or may be supplied to the chamber at any other desired point or plurality of points in this zone by well known means, not illustrated.

When chamber 5 is operated for the production of liquid residue, the latter may be withdrawn from the lower portion of this zone through line 62 and valve 63 to cooling and storage or elsewhere, as desired, and, as previously mentioned, regulated quantities of this material may, when desired, be directed, as previously described, to further treatment in heating coil 40.

When chamber 5 is operated for the production of petroleum coke as the final residual product of the process, it may be allowed to accumulate within this zone until the chamber has been substantially filled or until its operation is terminated for any other reason, following which the chamber may be cleaned and prepared for further operation. A plurality of coking chambers may, of course, be employed, when desired, although only a single chamber is shown in the drawing, and in such cases several chambers may be operated simultaneously or one or more chambers may be in operation while an-

other or others are being cleaned and prepared for further operation. Line 62 and valve 63 may also serve as a drain for chamber 5, and when coking is employed in this zone line 62 and valve 63 may serve as a means for introducing steam, water or other suitable cooling material into the chamber after its operation has been completed and preferably after it has been isolated from the rest of the system in order to hasten cooling and facilitate the removal of coke from this zone.

The preferred range of operating conditions which may be employed to accomplish the various objects of the present invention are approximately as follows: The heating coil to which the intermediate liquid conversion products of the process (reflux condensate) are supplied may utilize an outlet conversion temperature ranging, for example, from 900° to 1000° F., preferably with a superatmospheric pressure at this point in the system of from 100 to 500 pounds, or more, per square inch. Any desired pressure within substantially the same range may be employed in the succeeding chamber and the heating coil to which the vaporous products are supplied (after the removal of undesirable high-boiling components therefrom) preferably utilizes substantially the same or a somewhat lower pressure than that employed in said chamber with a temperature measured at the outlet from this heating coil ranging, for example, from 900° to 1100° F. When a substantial superatmospheric pressure of the order of 150 to 500 pounds, or more, per square inch is employed in the vapor heating coil, the conversion temperature employed therein is preferably of the order of 900° to 1000° F., and when lower pressures down to substantially atmospheric are employed in this zone, a higher temperature of the order of 975° to 1100° F. is preferred. The vaporizing and separating chamber succeeding the vapor heating coil is preferably operated at a relatively low pressure ranging, for example, from substantially atmospheric to 100 pounds, or thereabouts, per square inch, and this pressure may be either substantially equalized or somewhat reduced in the succeeding fractionating, condensing and collecting portions of the system. When viscosity-breaking operation is employed in the heating coil to which the heavy liquid products of the process are supplied, the temperature employed at the outlet from this zone may range, for example, from 760° to 850° F., preferably at a superatmospheric pressure of from 100 to 300 pounds, or thereabouts, per square inch. When subsequent coking of the high-boiling oils supplied to this zone is desired, the temperature employed at the outlet from the heating coil is preferably of the order of 925° to 1050° F., and the pressure employed in this zone may range from 25 to 350 pounds, or more, per square inch.

As a specific example of one of the many possible operations of the process, the charging stock which is supplied to the coking chamber comprises a Mid-Continent gas oil of about 32° A. P. I. gravity gas oil. Reflux condensate from the fractionator of the system is subjected in the first heating coil to an outlet conversion temperature of approximately 930° F. at a superatmospheric pressure of about 350 pounds per square inch, and the heated products are introduced into the coking chamber to which the charging stock is supplied, this zone being maintained at a superatmospheric pressure of ap-

proximately 100 pounds per square inch. After the removal of entrained heavy liquids from the vaporous products withdrawn from the coking chamber, the remaining vapors are subjected in a separate heating coil to an outlet conversion temperature of approximately 970° F., the pressure in this zone being substantially equalized with that in the coking chamber. The stream of heated products from the last-mentioned heating coil is cooled to a temperature of approximately 700° F. and introduced into a vaporizing and separating chamber operated at a superatmospheric pressure of approximately 50 pounds per square inch. The vaporous products from this zone are fractionated for the formation of said reflux condensate and the resulting fractionated vapors are condensed for recovery of desired motor fuel product of the process. The residual liquid products from the last-mentioned separating chamber are passed, together with said heavy liquids separated from the vaporous products from the coking zone, through a separate heating coil wherein they are quickly heated to an outlet conversion temperature of approximately 980° F. at a superatmospheric pressure of about 100 pounds per square inch and the heated products are introduced into the coking chamber. This operation will produce, per barrel of charging stock, approximately 64% of motor fuel having an octane number of approximately 72 by the motor method and approximately 55 pounds of relatively low volatile coke, suitable for sale as domestic fuel, the remainder being chargeable, principally, to uncondensable gas.

I claim as my invention:

1. A process for the conversion of hydrocarbon oils, which comprises subjecting intermediate liquid conversion products of the process to cracking temperature at a substantial superatmospheric pressure in a heating coil, introducing the heated products into an enlarged coking chamber wherein their high-boiling components are reduced to coke, introducing relatively cool hydrocarbon oil charging stock for the process into the coking chamber wherein it commingles with the hot conversion products and is thereby subjected to substantial vaporization, removing the commingled vaporous conversion products and vaporous components of the charging stock from the coking chamber, separating therefrom undesirable high-boiling liquids including entrained tars, pitches and similar materials of high coke-forming characteristics, subjecting the remaining vapors to cracking temperature under independently controlled heating conditions in a separate heating coil, cooling the resulting products sufficiently to prevent any substantial further conversion thereof and introducing the same into a vaporizing and separating chamber wherein vaporous and liquid conversion products are separated, subjecting the former to fractionation for the formation of reflux condensate comprising said intermediate liquid conversion products which are supplied for conversion to the first-mentioned heating coil, subjecting fractionated vapors of the desired end-boiling point to condensation, recovering the resulting distillate, subjecting liquid conversion products withdrawn from said vaporizing and separating chamber to additional conversion under non-coking conditions in another separate heating coil and introducing the resulting heated products into the coking chamber.

2. A process such as claimed in claim 1, wherein the heating coil to which said remaining va-

porous products from the coking chamber are supplied employs a maximum temperature of the order of 900° to 1000° F. with a superatmospheric pressure measured at the outlet therefrom of from 200 to 800 pounds per square inch.

3. A process such as claimed in claim 1, wherein the heating coil to which said remaining vaporous products from the coking chamber are supplied employs a maximum conversion temperature of from 975° to 1100° F. with a superatmospheric pressure measured at the outlet therefrom of from 100 pounds per square inch to substantially atmospheric pressure.

4. A process for the conversion of hydrocarbon oils which comprises subjecting intermediate liquid conversion products of the process to cracking temperature at a substantial superatmospheric pressure in a heating coil, introducing the resulting heated products into an enlarged chamber wherein separation of vaporous and liquid conversion products is accomplished, introducing relatively cool hydrocarbon oil charging stock for the process into said enlarged chamber wherein it commingles with the relatively hot conversion products and is thereby subjected to substantial vaporization, removing the commingled vaporous conversion products and vaporous components of the charging stock from said chamber, separating therefrom undesirable high-boiling components including any entrained tars, pitches and similar heavy liquids of a high coke-forming nature, subjecting the remaining vapors to cracking temperature under independently controlled heating conditions in a separate heating coil, cooling the resulting heated products sufficiently to prevent any substantial further conversion thereof and introducing the same into a vaporizing and separating chamber wherein their vaporous and liquid components are separated, subjecting the former to fractionation for the formation of reflux condensate comprising said intermediate liquid conversion products which are supplied for conversion to the first-mentioned heating coil, subjecting fractionated vapors of the desired end-boiling point to condensation, recovering the resulting distillate, subjecting residual liquid components withdrawn from said vaporizing and separating chamber to conditions of cracking temperature and superatmospheric pressure in a second separate heating coil regulated to effect a material reduction in the viscosity of the residual liquid without excessive coke and gas formation, introducing the resulting products into said enlarged chamber and recovering therefrom the final residual liquid product of the process.

5. A process such as claimed in claim 4, wherein regulated quantities of the liquid residue withdrawn from said enlarged chamber is returned for further treatment to the last-mentioned heating coil.

6. A process such as claimed in claim 4, wherein said heavy liquids removed from the vaporous products from said enlarged chamber are supplied for further treatment to the last-mentioned heating coil.

7. A process such as claimed in claim 4, wherein said heavy liquids removed from the vaporous products from said enlarged chamber are supplied to said vaporizing and separating chamber.

8. A process such as claimed in claim 4, wherein said enlarged chamber is operated at a sufficiently high superatmospheric pressure to effect appreciable continued conversion of the heated products supplied thereto in this zone.

9. A process such as claimed in claim 4, where-

in said enlarged chamber is operated at a substantially reduced pressure relative to that employed at the outlet from the first-mentioned heating coil.

5 10. A hydrocarbon oil conversion process which comprises heating reflux condensate, formed as hereinafter set forth, to cracking temperature under pressure in a heating coil and subsequently discharging the same into a separating chamber,
10 introducing relatively cool uncracked charging oil for the process to said chamber, removing commingled cracked vapors and charging oil vapors from the chamber and separating high-boiling fractions thereof, subjecting the remaining vapors
15 to cracking temperature under independently controlled conditions in a second heating zone, cooling the resultant products to below cracking temperature and separating the same into vaporous and liquid conversion products,
20 heating the liquid conversion products together with said high-boiling fractions to cracking temperature independently of said reflux condensate and said vapors and then introducing the same to said chamber, fractionating said vaporous conversion products and supplying resultant reflux condensate to said heating coil, and finally condensing the fractionated vapors.
25

11. A hydrocarbon oil conversion process which comprises heating reflux condensate, formed as hereinafter set forth, to cracking temperature under pressure in a heating coil and subsequently discharging the same into a separating chamber,
5 introducing relatively cool charging oil for the process to said chamber, removing commingled cracked vapors and charging oil vapors from the chamber and subjecting the same to cracking temperature under independently controlled conditions
10 in a second heating zone, cooling the resultant products to below cracking temperature and separating the same into vaporous and liquid conversion products, heating the liquid conversion products to cracking temperature independently
15 of said reflux condensate and said vapors and then introducing the same to said chamber, removing unvaporized oil from the chamber and heating the same to cracking temperature together with said liquid conversion products,
20 fractionating said vaporous conversion products and supplying resultant reflux condensate to said heating coil, and finally condensing the fractionated vapors.

JACQUE C. MORRELL.