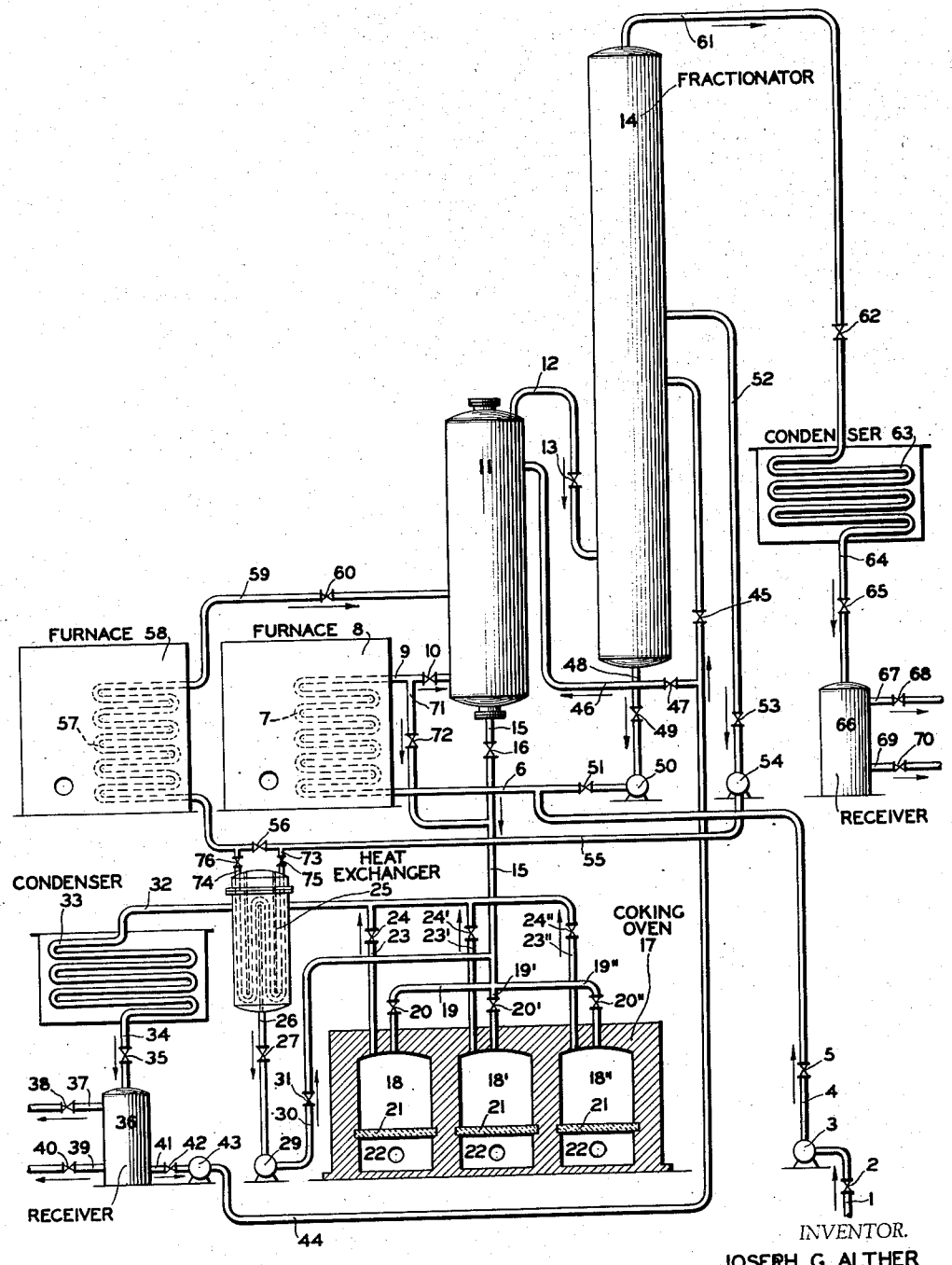
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CONVERSION AND COKING OF HYDROCARBON OILS

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CONVERSION AND COKING OF HYDROCARBON OILS

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This invention particularly refers to an improved process for the treatment of solid or semi-solid carbonaceous materials, such as coal, peat, lignite, oil shales and the like, admixed in finely divided form with hydrocarbon oil for the purpose of producing low-boiling distillates such as motor fuel of high antiknock value and low-volatile coke.

One specific embodiment of the invention comprises subjecting a mixture of finely divided solid or semi-solid carbonaceous material, such as coal, and hydrocarbon oil to relatively mild conversion temperature at superatmospheric pressure in a heating coil, introducing the heated products into a reduced pressure vaporizing chamber wherein the vaporous and residual conversion products separate, subjecting vaporous conversion products to fractionation, whereby their components boiling above the range of the desired final light distillate product of the process are condensed as reflux condensate, separating the reflux condensate into low-boiling and high-boiling fractions, returning said high-boiling fractions to the heating coil for further conversion, together with the charging stock mixture, subjecting said low-boiling fractions of the reflux condensate to further conversion under independently controlled more severe conversion conditions in a separate heating coil, introducing the highly heated products into said vaporizing chamber, withdrawing unvaporized residual conversion products from said vaporizing chamber and introducing the same into alternately operated low-pressure coking ovens wherein they are passed over highly heated non-metallic surfaces and reduced to coke, which is allowed to accumulate thereon in a relatively thin layer, separating heavy tars and similar high coke-forming materials from the volatiles evolved by the coking operation, subjecting the remaining vapors from the coking zone to condensation, collecting and separating the resulting distillate and gas and commingling the distillate with said vaporous conversion products subjected to said fractionation whereby the distillate is subjected to the same treatment afforded said vaporous conversion products.

Various modifications of the specific embodiment of the invention above described may be employed without departing from the scope of the present invention. Some of these modifications which, however, are not to be considered equivalent to the operation disclosed in the foregoing specific embodiment, are described in connection with the following description of the accompanying drawing. The drawing, which is diagrammatic, illustrates one specific form of apparatus, including provisions for some of the modifications described, permitting operation of the process in accordance with the invention.

Referring to the drawing, charging stock for the process, comprising finely divided solid or semi-solid carbonaceous material such as above mentioned, preferably in finely divided form and thoroughly mixed with hydrocarbon oil, is supplied from any suitable mixing device, not shown, through line 1 and valve 2 to pump 3 by means of which it is fed through line 4, valve 5 and line 6 to heating coil 7. The charging stock may, of course, be preheated in any well known manner, not shown in the drawing, prior to its introduction into the heating coil, when so desired.

A furnace 8 of any suitable form supplies the required heat to the charging stock mixture passing through heating coil 7 to bring it to the desired conversion temperature. Preferably a substantial superatmospheric pressure is employed at the outlet from the heating coil and the velocity of the material passing through the heating coil and the rate of heating to which it is subjected are so controlled that the material is not allowed to remain under conversion conditions in this zone for a sufficient length of time to permit any appreciable coke formation and deposition in the heating coil.

The heated products are discharged from heating coil 7 through line 9 and valve 10 into vaporizing chamber 11, the pressure imposed upon the heated products preferably being substantially reduced as they pass through valve 10 in order to reduce their temperature and arrest conversion or retard it sufficiently to prevent coking in chamber 11. The reduced pressure conditions employed in chamber 11 also affect further vaporization of the liquid conversion products from the heating coil by virtue of the latent heat liberated from the conversion products. The vaporous and unvaporized residual conversion products separate in chamber 11, the vapors passing, in the case illustrated, from the upper portion of this zone through line 12 and valve 13 to be subjected to fractionation in fractionator 14.

The unvaporized residue is withdrawn from the lower portion of chamber 11 through line 15 and valve 16 to coking oven 17 comprising, in the case illustrated, a plurality of alternately operated coking chambers 18, 18' and 18'' into which the residue is introduced through lines 19, 19' and 19'' respectively, controlled by the respective valves 20, 20' and 20''. When desired, particularly in case the oil supplied to heating coil 7 is of an ex-

ceptionally heavy high coke-forming nature, the heated oil in this zone instead of being supplied to chamber 11 may be supplied directly to the coking oven by means of line 71, valve 72, line 15, lines 19, 19' and 19'' and the respective valves 20, 20' and 20''. Preferably, however, when the nature of the charging stock permits the heated oil from heating coil 7 is subjected to further vaporization at reduced pressure in chamber 11, prior to coking of the residual products. The residue supplied to the coking chambers passes over highly heated surfaces 21, preferably comprised of suitable ceramic material of high heat conductivity, such as silicon carbide, aluminum oxide or the like, heated from beneath by means of heat derived from the combustion of fuel in combustion zones 22. The coke is allowed to accumulate on the highly heated surfaces 21 to a depth of approximately 6 inches or less, following which the chamber is isolated from the system and the coke removed therefrom in any well known manner, not illustrated, while coking of the residue from chamber 11 is continued in another coking chamber.

Volatiles derived from the residue by the coking operation pass from chambers 18, 18' and 18'' through the lines 23, 23' and 23'', respectively, controlled by the respective valves 24, 24' and 24'' and pass, in the case illustrated, through heat exchanger or partial condenser 25 wherein they are cooled sufficiently to condense and remove therefrom the tars and similar heavy components of high coke-forming characteristics. These heavy components are withdrawn from the lower portion of heat exchanger 25 through line 26 and may be removed, all or in part, from the system to storage or elsewhere, as desired, by well known means not shown, or, preferably, may pass through valve 27 to pump 29 by means of which they are returned through line 30 and valve 31 to the coking zone entering the coking chambers through lines 19, 19' and 19'' controlled by valves 20, 20' and 20'', respectively, in the manner previously described.

Vaporous products from the coking operation which remain uncondensed in heat exchanger 25 and pass therefrom through line 32 to cooling and condensation in condenser 33, from which the resulting distillate and uncondensable gas pass through line 34 and valve 35 to collection and separation in receiver 36. Uncondensable gas may be released from the receiver through line 37 and valve 38. Distillate may be withdrawn from this zone to storage or to any desired further treatment through line 39 and valve 40. Preferably, however, at least a portion of the distillate collected in receiver 36 is withdrawn therefrom through line 41 and valve 42 to pump 43 by means of which it is fed through line 44, passing either through valve 45 in this line into fractionator 14 or through line 46 and valve 47 into vaporizing chamber 11, commingling in either case with the vaporous conversion products subjected to fractionation. Any distillate from receiver 36 supplied to chamber 11 may be utilized as a means of cooling the vapors leaving this zone sufficiently to effect the removal therefrom of entrained residual material, preventing its passage with the vapors to fractionator 14 and subsequent return to the heating coil. When desired, fractionating means of any suitable form may be employed in the upper portion of chamber 11 to assist in the removal of any high-boiling deleterious materials from the vapors supplied to fractionator 14 and to obtain intimate contact between the vapors and the cooling medium. The distillate thus utilized in chamber 11 is substantially vaporized in this zone and passes through line 12 and valve 13 to fractionator 14, together with the vaporous conversion products from the vaporizing chamber. Any distillate supplied from receiver 36 to fractionator 14 is introduced, in the case illustrated, into direct contact with the vapors undergoing fractionation in this zone, serving as a cooling medium to assist fractionation of the vapors and being itself substantially vaporized by contact therewith and subjected to the same fractionation afforded the vapors from chamber 11.

Any other desired form of heat exchanger or partial condenser, not illustrated may, of course, be employed in place of heat exchanger 25 or, when desired, the use of this zone may be dispensed with, in which case the total vapors from the coking zone are preferably supplied, by well known means, not shown in the drawing, to chamber 11 wherein the heavy tars and similar high coke-forming materials may separate from the lower boiling vapors, to be returned to the coking zone with the other residual products from chamber 11, while the remaining vapors pass to fractionator 14. Heat exchanger 25 or its equivalent may also be dispensed with when the distillate from receiver 36 is returned, as previously described, to chamber 11.

Components of the materials supplied to fractionator 14 boiling above the desired final light distillate product of the process are condensed by fractionation in this zone as reflux condensate and the reflux condensate is separated into low-boiling and high-boiling fractions. Fractionated vapors of the desired end-boiling point are withdrawn from the upper portion of fractionator 14, together with uncondensable gas from this portion of the system, through line 61 and valve 62 to condensation and cooling in condenser 63. The resulting distillate and uncondensable gas passes through line 64 and valve 65 to collection and separation in receiver 66. Uncondensable gas may be released from the receiver through line 67 and valve 68. Distillate may be withdrawn from this zone to storage or to any desired further treatment through line 69 and valve 70. When desired, a portion of the distillate collected in receiver 66 may be returned, by well known means not shown in the drawing, to the upper portion of fractionator 14 to assist fractionation in this zone and to maintain the desired vapor outlet temperature therefrom, thereby controlling the end-boiling point of the final light distillate product of the process.

High-boiling fractions of the reflux condensate which collect within the lower portion of fractionator 14 are withdrawn therefrom through line 48 and valve 49 to pump 50 by means of which they are returned through line 6 and valve 51 to further conversion in heating coil 7, together with the charging stock mixture supplied to this zone, as previously described. The low-boiling fractions of the reflux condensate are withdrawn as a side stream from any suitable point or plurality of points in the fractionator, for example, through line 52 and valve 53 to pump 54 by means of which they may be supplied through line 55 and valve 56 to further conversion in heating coil 57. Provision is made in the case here illustrated for passing the low-boiling reflux condensate in indirect heat exchange relation with the vaporous products from the coking zone in heat exchanger 25 by means of lines 73 and 74

controlled respectively by valves 75 and 76, serving as the cooling medium to assist removal of the high coke-forming materials from the vapors and being thereby preheated, prior to its introduction into heating coil 57.

Heating coil 57 is located within a furnace 58 of any suitable form and the heat derived within the furnace is utilized to heat the oil passing through the heating coil preferably to a higher conversion temperature than that employed in heating coil 7 and preferably at substantial superatmospheric pressure. The heated products pass from heating coil 57 through line 59 and valve 60 into vaporizing chamber 11, the pressure preferably being substantially reduced as the oil passes through valve 60.

Owing to the low-boiling character of the oil supplied to heating coil 57 the desired degree of conversion for this material may ordinarily be obtained in the heating coil without the danger of excessive coke formation and deposition in this zone such as would result from the treatment of heavier oils for a comparable length of time in the heating coil. However when, for any reason, it is desired to shorten the conversion time in the heating coil and to subject the vaporous conversion products from this zone to continued conversion for a predetermined time and employ a shorter time or no appreciable continued conversion time for the liquid products, the materials from heating coil 57 may be passed through a reaction chamber of suitable well known form, not illustrated, which is preferably maintained at substantially the same pressure as that employed at the outlet from the heating coil and is preferably well insulated to prevent the excessive loss of heat by radiation. When such a zone is employed the preferred form is a vertically disposed elongated chamber in which the vapors may pass either upward or downward through the chamber and be subjected to continued conversion time during their passage therethrough while the liquid conversion products are quickly withdrawn from the lower portion of the chamber to vaporizing chamber 11 or direct to the coking zone, the vapors passing, all or in part, either direct to fractionator 14 or into chamber 11.

The products from heating coil 57, or from the subsequent reaction chamber when such a zone is employed, supplied to chamber 11 are commingled with and subjected to the same treatment, already described, as that afforded the heated products from heating coil 7.

In an apparatus such as illustrated and above described the preferred operating conditions are approximately as follows: The heating coil to which the charging stock and high-boiling condensate from the fractionator are supplied may employ a conversion temperature ranging, for example, from 800 to 950° F. measured at the outlet therefrom, and preferably a substantial superatmospheric pressure of the order of 100 to 500 pounds, or more, per square inch, is employed at this point but is substantially reduced in the succeeding vaporizing chamber to a pressure which may range, for example, from 100 pounds per square inch to substantially atmospheric pressure, a substantially equalized or somewhat reduced pressure within this same range may be employed in the fractionating, condensing and collecting portions of the system. The coking zone may be operated at any desired pressure ranging from subatmospheric to low superatmospheric pressure, preferably not in excess of 50 pounds, or thereabouts, per square inch when a coking oven of the type illustrated is employed. Coking temperatures employed may range from 1000 to 1500° F., or more. The low-boiling oils supplied to the second heating coil of the system are preferably subjected to a conversion temperature, measured at the outlet from this zone, of the order of 900 to 1050° F. and preferably a superatmospheric pressure of from 200 to 800 pounds, or more, per square inch, is employed at this point in the system, although lower pressures down to substantially atmospheric may be used, when desired.

As a specific example of the operation of the process of the present invention, as it may be practiced in an apparatus such as illustrated and above described, the charging stock may comprise a mixture of about equal parts by weight of fuel oil and pulverized bituminous coal having a volatile content of approximately 38 percent. This mixture is subjected, together with the heavy condensate from the fractionator of the system to a conversion temperature of approximately 890° F. at a superatmospheric pressure of about 250 pounds per square inch, a pressure of about 50 pounds per square inch being maintained in the succeeding vaporizing chamber, the resulting residue being coked at substantially atmospheric pressure with a temperature of approximately 1200° F. in the coking zone. Heavy high coke-forming materials are removed from the vapors resulting from the coking operation and are returned to the coking zone, the remaining vapors are subjected to condensation and the distillate is returned, in part, to the vaporizing chamber and, in part, to the fractionator as cooling and refluxing material. Low-boiling reflux condensate from the fractionator is separately subjected to a conversion temperature of approximately 950° F. at a superatmospheric pressure of about 500 pounds per square inch measured at the outlet from the heating coil. This operation will yield, per ton of charging stock, about 130 gallons of motor fuel having an antiknock value equivalent to an octane number of approximately 72, about 900 pounds of low volatile coke, comprising a mixture of petroleum coke and coke resulting from the carbonization of coal, and about 2500 cubic feet of uncondensable gas of good calorific value.

I claim as my invention:

1. A process for the conversion and coking of mixtures of hydrocarbon oil and finely divided carbonaceous material which comprises, subjecting the mixture to conversion temperature at superatmospheric pressure while flowing in a restricted stream through a heating zone, separating the resulting vaporous products and nonvaporous residual products at substantially reduced pressure in a separating zone, removing the residue from the separating zone and subjecting it to coking, condensing the vapors evolved by the coking and introducing resultant condensate to the separating zone, 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 the resulting distillate, separating the reflux condensate into low-boiling and high-boiling fractions, returning the latter to said heating zone, together with the charging stock mixture and separately subjecting said low-boiling fractions to more severe conversion conditions than said mixture and then introducing the same to the separating zone.

2. A process for the conversion and coking of mixtures of hydrocarbon oil and finely divided carbonaceous material which comprises, subjecting the mixture to conversion temperature at superatmospheric pressure in a heating coil, introducing the heated materials into a reduced pressure vaporizing chamber wherein the vaporous conversion products and non-vaporous residual conversion products separate, subjecting the vapors to fractionation whereby their insufficiently converted components are condensed as reflux condensate, subjecting fractionated vapors of the desired end-boiling point to condensation, recovering the resulting distillate, introducing non-vaporous residue from the vaporizing chamber into a coking zone, wherein it is reduced to coke by passing the same over a highly heated non-metallic surface upon which the coke is allowed to accumulate in a relatively thin layer, subjecting vaporous products from the coking operation to partial condensation whereby tars and similar high-boiling materials are separated therefrom, returning the latter to the coking zone for further treatment, subjecting the remaining vapors to condensation, recovering the resulting distillate, commingling said distillate from the coking operation with said vaporous conversion products whereby they are subjected to fractionation therewith, separating the reflux condensate formed by such fractionation into low-boiling and high-boiling fractions, returning the latter to the heating coil for further conversion, together with the charging stock mixture, subjecting said low-boiling fractions to independently controlled more severe conversion conditions of elevated temperature and superatmospheric pressure in separate heating coil and introducing the heated products into said vaporizing chamber.

3. A combined cracking and coking operation which comprises heating a mixture of hydrocarbon oil and solid carbonaceous material to relatively mild conversion temperature while flowing in a restricted stream through a heating zone, separating the heated mixture into vapors and residue in a separating zone, removing the residue from the separating zone and reducing the same to coke in a coking zone, condensing the vapors evolved in the coking zone independently of the initially separated vapors and introducing resultant condensate into contact with the initially separated vapors, fractionating the latter and separating relatively heavy and light reflux condensates therefrom, returning such heavier reflux condensate to the heating zone, heating the lighter reflux condensate in a second heating zone to higher conversion temperature than the mixture in the first-mentioned heating zone and then introducing the same to the separating zone, and finally condensing the fractionated vapors.

4. A combined cracking and coking operation which comprises heating a mixture of hydrocarbon oil and solid carbonaceous material to relatively mild conversion temperature while flowing in a restricted stream through a heating zone, separating the heated mixture into vapors and residue in a separating zone, removing the residue from the separating zone and reducing the same to coke in a coking zone, condensing the vapors evolved in the coking zone and introducing resultant condensate into the separating zone without prior heating thereof to cracking temperature, fractionating the vapors from the separating zone and separating relatively heavy and light reflux condensates therefrom, returning such heavier reflux condensate to the heating zone, heating the lighter reflux condensate in a second heating zone to higher conversion temperature than the mixture in the first-mentioned heating zone and then introducing the same to the separating zone, and finally condensing the fractionated vapors.

5. A combined cracking and coking operation which comprises heating a mixture of hydrocarbon oil and solid carbonaceous material to relatively mild conversion temperature while flowing in a restricted stream through a heating zone, separating the heated mixture into vapors and residue in a separating zone, removing the residue from the separating zone and reducing the same to coke in a coking zone, condensing vapors evolved in the coking zone independently of the initially separated vapors thereby forming condensate, fractionating the first-named vapors in contact with at least a portion of said condensate and supplying liquid products of this fractionation to the heating zone, further fractionating the remaining vapors to form a relatively light reflux condensate, heating such light reflux condensate in a second heating zone to higher conversion temperature than the mixture in the first-mentioned heating zone and then introducing the same to the separating zone, and finally condensing the fractionated vapors.

6. A process for the conversion and coking of mixtures of hydrocarbon oil and finely divided carbonaceous material which comprises, subjecting the mixture to conversion temperature at super-atmospheric pressure in a heating coil, introducing the heated materials into a reduced pressure vaporizing chamber wherein the vaporous conversion products and non-vaporous residual conversion products separate, subjecting the vapors to fractionation whereby their insufficiently converted components are condensed as reflux condensate, subjecting fractionated vapors of the desired end-boiling point to condensation, recovering the resulting distillate, introducing non-vaporous residue from the vaporizing chamber into a coking zone, wherein it is reduced to coke, subjecting vaporous products from the coking operation to partial condensation whereby tars and similar high-boiling materials are separated therefrom, returning the latter to the coking zone for further treatment, subjecting the remaining vapors to condensation, recovering the resulting distillate, commingling said distillate from the coking operation with said vaporous conversion products whereby they are subjected to fractionation therewith, separating the reflux condensate formed by such fractionation into low-boiling and high-boiling fractions, returning the latter to the heating coil for further conversation, together with the charging stock mixture, subjecting said low-boiling fractions to independently controlled more severe conversion conditions of elevated temperature and super-atmospheric pressure in separate heating coil and introducing the heated products into said vaporizing chamber.

7. A combined cracking and coking operation which comprises heating a mixture of hydrocarbon oil and solid carbonaceous material to relatively mild conversion temperatures while flowing in a restricted stream through a heating zone, separating the heated mixture into vapors and residue in a separating zone, removing the residue from the separating zone and reducing the same to coke in a coking zone, partially condensing the vapors evolved in the coking zone independently of the first-named vapors to sepa-

rate tars and similar high-boiling materials therefrom and returning such separated materials directly to the coking zone, subjecting the second-mentioned vapors to further condensation and introducing resultant condensate to the separating zone, fractionating the vapors from the separating zone and separating relatively heavy and light reflux condensates therefrom, returning such heavier reflux condensate to the heating zone, heating the lighter reflux condensate in a second heating zone to higher conversion temperature than the mixture in the first-mentioned heating zone and then introducing the same to the separating zone, and finally condensing the fractionated vapors.

8. A combined cracking and coking operation which comprises heating a mixture of hydrocarbon oil and solid carbonaceous material to relatively mild conversion temperatures while flowing in a restricted stream through a heating zone, separating the heated mixture into vapors and residue in a separating zone, removing the residue from the separating zone and reducing the same to coke in a coking zone, partially condensing the vapors evolved in the coking zone independently of the first-named vapors to separate tars and similar high-boiling materials therefrom and returning such separated materials directly to the coking zone, combining constituents uncondensed by said partial condensation, without prior heating thereof to cracking temperature, with the first-named vapors and fractionating the resultant mixture to form relatively heavy and light reflux condensates therefrom, returning such heavier reflux condensate to the heating zone, heating the lighter reflux condensate in a second heating zone to higher conversion temperature than the mixture in the first-mentioned heating zone and then introducing the same to the separating zone, and finally condensing the fractionated vapors.

9. The process as defined in claim 8 further characterized in that said constituents are combined with said first-named vapors by introduction thereof to the separating zone.

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