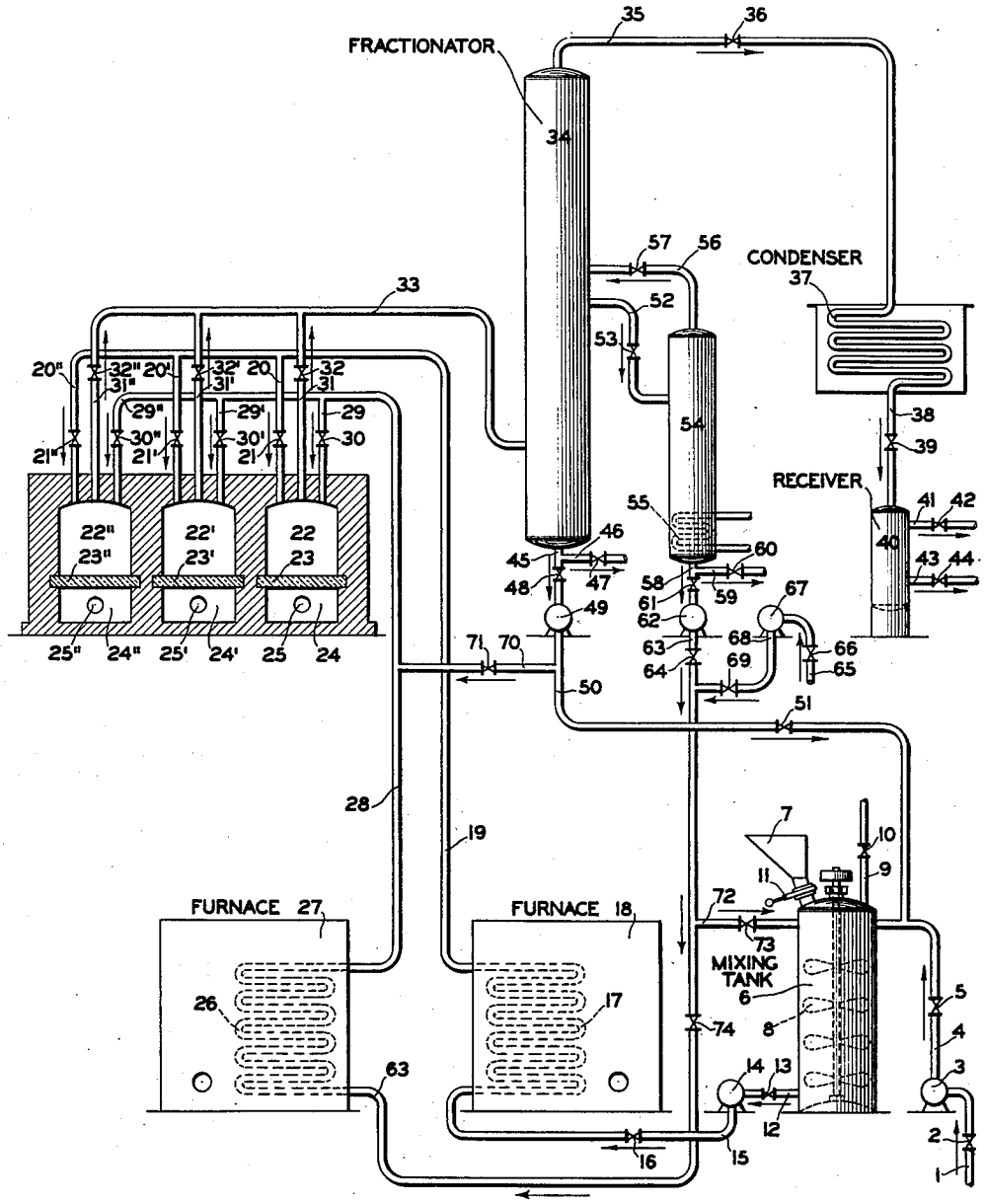
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TREATMENT OF HYDROCARBONS

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TREATMENT OF HYDROCARBONS

Joseph G. Alther, Chicago, Ill., assignor to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

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This invention particularly refers to an improved process for the pyrolytic conversion and coking of mixtures of solid bituminous materials, such as coal, in liquid hydrocarbons, such as petroleum.

Processes have previously been proposed for the pyrolytic conversion of mixtures of hydrocarbons, such as coal and oil, accompanied by reduction of the residual conversion products to coke in alternately operated coking ovens wherein the residue is passed over the surface of highly heated suitable refractory material, heated from beneath, in such a manner that there is no contact between furnace gases resulting from combustion of the materials utilized to furnish the heat and the hydrocarbon vapors and gases evolved during the coking operation. In such processes the coke is allowed to accumulate upon the hot refractory surface and additional residue is supplied thereto until the coke layer is built up to a depth of several inches, following which the residue is diverted to another oven where the coking operation is continued while the coke accumulation is removed from the first oven by means of an hydraulic ram or in any other suitable manner and the oven is prepared for further operation. Obviously, after the first film of coke is deposited on the heating surface the heat required to coke the incoming residue must pass through the accumulated coke layers which continue to build up upon the heating surface as the operation progresses. This, of course, places a severe restriction upon the depth of coke bed which may be built up upon the heating surface in each operation of any single oven, if any substantial degree of uniformity is to be maintained in the character of the coke produced, and necessitates frequent cleaning of the ovens.

The present invention provides an improvement to the general type of process above described whereby heating of the residual conversion products of the process to effect their reduction to coke is accomplished from above as well as from beneath the surface upon which the coke is allowed to accumulate. This is accomplished by introducing a stream of highly heated hydrocarbon oil, of lower average boiling range than the residual oil, into the coking ovens above the coke bed, whereby the highly heated materials come into direct contact with the upper surface of the residue undergoing coking; said highly heated materials being introduced into the coking ovens at a temperature sufficient to materially assist the coking operation.

The advantages of subjecting the material undergoing treatment to heating from opposite sides instead of passing substantially all of the heat required for the coking operation through an accumulated mass of coke will be apparent to those familiar with the art. By use of the features of the present invention a higher rate of coking may be obtained and a coke deposit of more uniform character throughout its mass will result. Also, when desired, a thicker layer of coke may be built up upon the refractory heating surface than can be satisfactorily coked when all of the heat is supplied through this refractory material and through the accumulated coke layer. Also, in the present invention the highly heated stream of hydrocarbon oil introduced into the coking ovens will commingle therein with the other vaporous products in this zone, including the volatiles evolved from the residual material during the coking operation, serving to heat the same to a temperature sufficient to effect their substantial further conversion for the production of additional yields of desirable light products such as motor fuel of high anti-knock value.

It should be further noted that by use of the features of the present invention all of the advantages of coking ovens of the general type above described are retained and the disadvantages arising from passing heat through the layer of accumulated coke upon the refractory heating surface are minimized.

In one of its preferred forms the invention provides for utilizing a selected low-boiling fraction of the reflux condensate, which comprises the insufficiently converted intermediate products of the process recovered from the vaporous conversion products by fractionation, as the oil which is heated to a high conversion temperature and introduced into the coking ovens to supply a substantial proportion of the heat required for the coking operation. Separate treatment of a selected fraction of the reflux condensate under independently controlled more severe conversion conditions than those to which the charging stock and/or higher boiling fractions of the reflux condensate are subjected is in itself a feature of recognized advantage over the practice of returning this material to further conversion, together with the charging stock and/or higher boiling fractions of the reflux condensate, and while this constitutes only one specific means of accomplishing the purpose of the invention its cooperative nature makes it particularly desirable. It is, of course, within the scope of the invention to employ any other suitable oil from within the system or from any desired external source as the

heat carrying medium supplied to the coking ovens, either alone or in conjunction with the use of a selected fraction of the reflux condensate for this purpose.

One embodiment of the invention comprises subjecting a mixture of coal and hydrocarbon oil to conversion temperature at superatmospheric pressure in a heating coil, introducing the heated products into a coking oven, wherein their non-vaporous components are reduced to coke upon a refractory surface, heated to a high temperature from beneath, whereon the coke is allowed to accumulate, subjecting vaporous products from the coking oven to fractionation whereby their components boiling above the range of the final light distillate product of the process are condensed as reflux condensate, subjecting fractionated vapors of the desired end-boiling point to condensation, collecting and separating the resulting distillate and gas, simultaneously subjecting another hydrocarbon oil of lower boiling characteristics to independently controlled more severe conversion conditions of elevated temperature and superatmospheric pressure in a separate heating coil and introducing the highly heated products from said separate heating coil into the coking oven above the mass of accumulated coke therein for the purpose of supplying additional heat to the upper surface of the material undergoing coking.

The accompanying diagrammatic drawing illustrates one specific form of apparatus in which the invention can be practiced.

Hydrocarbon oil charging stock such as fuel oil, residual oil, tars, pitches, cracked residue, natural or artificial asphalts and the like, may be supplied through line 1 and valve 2 to pump 3 by means of which it is fed through line 4 and valve 5 into a mixing tank 6 of any suitable form. Solid or semi-solid bituminous material such as, for example coal, peat, lignite, gilsonite or the like is supplied to mixing tank 6, preferably in finely divided form, through a suitable charging hopper 7 and the liquid and solid or semi-solid components of the charging stock are thoroughly admixed in any suitable manner, for example, by means of a stirring device such as indicated at 8, motivated by any suitable means (not shown).

The liquid components of the charging stock may, when desired, be supplied to mixing tank 6 in heated state and/or, when desired, mixing tank 6 may be heated by means of a steam jacket (not shown), or in any other suitable manner in order to assist in maintaining the fluidity of the charging stock. In such cases a superatmospheric pressure may, when desired, be maintained in mixing tank 6 to prevent excessive vaporization of the charging stock and any excess of evolved vapors may be liberated from the mixing tank through line 9, controlled by valve 10. Also, when superatmospheric pressure is employed in the mixing tank a suitable valve, for example, such as indicated at 11, may be provided beneath hopper 7.

The charging stock mixture is withdrawn in thoroughly commingled state from mixing tank 6 through line 12 and valve 13 to pump 14 by means of which it is fed through line 15 and valve 16 to heating coil 17.

A furnace 18 of any suitable form supplies the required heat to the materials passing through heating coil 17 to bring them to the desired conversion temperature, preferably at a substantial superatmospheric pressure, and the heated products are discharged from the heating coil through line 19 and pass through lines 20, 20' and 20'', controlled by the respective valves 21, 21' and 21'' into the respective coking ovens 22, 22' and 22''.

Coking ovens 22, 22' and 22'' are similar coking zones, preferably operated at substantially atmospheric or relatively low superatmospheric pressure, wherein the non-vaporous components of the materials supplied thereto come into contact with the hot upper surface of refractory surfaces 23, 23' and 23'', which are heated from beneath by the combustion of any suitable form of fuel supplied to combustion zones 24, 24' and 24'' by means of any suitable form of burners (not shown) through burner ports 25, 25' and 25''. The non-vaporous materials are reduced to coke in the coking ovens and the coke is allowed to accumulate upon the highly heated refractory surfaces 23, 23' and 23''. Heat for the coking operation is continuously supplied through the refractory plates and through the accumulated layers of coke to the uncoked non-vaporous materials which are continuously supplied to the coking ovens and, in the present invention, a substantial proportion of the heat required for the coking operation is derived from more highly heated conversion products than those supplied from heating coil 17, which latter are introduced into the coking ovens from heating coil 26 through line 28 and through lines 29, 29' and 29'', controlled by the respective valves 30, 30' and 30''; said highly heated conversion products being introduced to the coking ovens above the mass of coke and materials undergoing coking accumulated upon the highly heated refractory plates in such a manner as to supply heat to the upper surface of the mass.

It will be understood that although three coking ovens are illustrated in the drawing one or any desired number of such zones may be employed and, preferably, when a plurality is employed they are alternately operated; a layer of coke of predetermined thickness being allowed to accumulate upon the heated refractory plate in one or more of the ovens, following which the supply of combustible fuel and the supply of conversion products thereto is discontinued, the conversion products being diverted to one or a plurality of similar ovens wherein the coking operation continues while the coke deposit is removed from the oven or ovens which have been isolated from the system by means of an hydraulic ram or in any other suitable manner (not shown), whereupon the ovens are prepared for further operation.

Vaporous products including the vaporous conversion products supplied to the coking ovens from the heating coils and volatiles evolved during the coking operation are removed from coking ovens 22, 22' and 22'' by means of the respective lines 31, 31' and 31'', controlled by the respective valves 32, 32' and 32'' and pass through line 33 to fractionator 34.

The components of the vaporous products supplied to fractionator 34 boiling below the range of the final light distillate product of the process are condensed in this zone as reflux condensate, which may be removed, all or in part, from the system or subjected to further treatment therein, as will be later more fully described, and fractionated vapors of the desired end-boiling point are withdrawn from the upper portion of the fractionator through line 35 and valve 36 to be subjected to condensation and cooling in condenser 37. The resulting distillate and gas passes

through line 38 and valve 39 to collection and separation in receiver 40. Uncondensable gas may be released from the receiver through line 41 and valve 42. The distillate may be withdrawn from receiver 40 through line 43 and valve 44 to storage or to any desired further treatment. When desired, a regulated portion of the distillate collected in receiver 40 may be recirculated, by well known means (not shown) to the upper portion of fractionator 34 to serve as a cooling and refluxing medium to assist fractionation of the vaporous products in this zone and to maintain the desired vapor outlet temperature from the fractionator.

The total reflux condensate recovered from the vaporous products in fractionator 34 may be allowed to collect in the lower portion of fractionator 34, from which it is withdrawn through line 45, and may be removed, all or in part, from the system through line 46 and valve 47 to cooling and storage or to any desired further treatment or may pass, all or in part, through valve 48 in line 45 to pump 49, by means of which it may be supplied through line 50 and valve 51 to mixing tank 6, to commingle with the other components of the charging stock mixture supplied to this zone and be supplied therewith to heating coil 17, as previously described or, when desired, this material may be supplied direct to heating coil 17 by well known means (not shown).

As an alternative to the disposition of the reflux condensate above described, which latter constitutes a preferred feature of the invention, only high-boiling fractions of the reflux condensate are collected within the lower portion of fractionator 34 and returned therefrom to mixing tank 6 or to heating coil 17 or withdrawn, all or in part, from the system, in the manner previously described, while selected low-boiling fractions of the reflux condensate are withdrawn from a suitable intermediate point or plurality of points in fractionator 34, for example, through line 52 and valve 53, to column 54 wherein they may be subjected to reboiling to free the same of any entrained gases and low-boiling components within the range of the desired overhead product from the fractionator. The reboiling may be accomplished by circulating a suitable heating medium such as steam, hot oil or the like through reboiler coil 55 located in the lower portion of column 54 or in any other suitable manner (not shown). The vapors evolved by the reboiling operation in column 54 may be returned to fractionator 34 by means of line 56 and valve 57. The stabilized low-boiling fraction of the reflux condensate is withdrawn from the lower portion of column 54 through line 58 and may be withdrawn, all or in part, from the system to cooling and storage or elsewhere, as desired, through line 59 and valve 60. Preferably, however, a portion or all of this material passes through valve 61 in line 58 to pump 62 by means of which it is supplied through line 63, valve 64 and valve 74 to further conversion in heating coil 26.

It is also within the scope of the invention to supply a relatively low-boiling oil from any desired external source to conversion in heating coil 26, either alone or together with the low-boiling fraction of the reflux condensate from fractionator 34. Any suitable type of oil, including such materials as gas oil, kerosene or kerosene distillate, pressure distillate or pressure distillate bottoms, naphtha, straight-run gasoline or other motor fuel of interior anti-knock quality or mixtures of such oils, may be employed and may be supplied from the system by means of line 65, valve 66, pump 67, line 68 and valve 69. When low-boiling oil of the nature described is supplied to heating coil 26 it may comprise a secondary charging stock or may, when desired, comprise the only liquid charging stock supplied to the system. In the latter case the operation of the process may be started by first cracking only said low-boiling liquid charging stock until a sufficient quantity of high-boiling reflux condensate is being produced to furnish the material to be commingled with the solid or semi-solid charging stock in mixing tank 6, for treatment in heating coil 17, or, when desired, the operation may be started by employing suitable heavy oil from an external source to commingle with the solid or semi-solid charging stock, said heavy oil being gradually replaced as the operation progresses by reflux condensate or high-boiling fractions of the reflux condensate from fractionator 34.

It is also within the scope of the invention, when desired, to separate only heavy tars, pitches and similar high coke-forming materials from the vaporous products supplied to fractionator 34 in the lower portion of this zone and to return said high coke-forming materials to the coking ovens, for example, by means of line 70, valve 71, line 28 and lines 29, 29' and 29'' controlled by the respective valves 30, 30' and 30'', in which case the remaining components of the vapors condensed in fractionator 34 as reflux condensate may be returned, as desired, either to heating coil 26 or to heating coil 17. The return of such material to heating coil 17 may be accomplished by diverting the condensate withdrawn, for example, as a side stream from fractionator 34 at any suitable point or plurality of points in this zone, as previously described, from line 63 through line 72 and valve 73 into mixing tank 6 or by supplying the same by well known means (not shown) direct to heating coil 17.

As another alternative method of operation other well known means, not illustrated in the drawing, such as, for example, a tar separator interposed in vapor line 33 between the coking ovens and fractionator 34 may be employed to remove the high coke-forming materials from the vapors, suitable lines and a pump (not shown) being employed to return said high coke-forming materials to the coking ovens while the remaining components of the vapors are separated in fractionator 34, as previously described, into low boiling and high boiling fractions, the low boiling fractions preferably being returned to heating coil 26 and the high boiling fractions to heating coil 17.

It will be understood, of course, that the various alternative methods of operation above described are not equivalent but that the methods of operation may be varied to suit requirements. Other departures from the exact methods of operation above described will be apparent to those skilled in the art and are entirely within the spirit and scope of the invention.

In an apparatus such as illustrated and above described, the preferred range of operating conditions is approximately as follows:

The temperature employed at the outlet from the heating coil to which the mixture of liquid and solid or semi-solid material is supplied is preferably within the range of 800 to 900° F., or thereabouts, and a substantial superatmospheric pressure within the range of 100 to 500 pounds, or thereabouts, per square inch is preferred at

this point in the system although, when desired, milder conditions, below those at which any substantial conversion of the charging stock will occur, may be employed in this zone. Substantially atmospheric, sub-atmospheric or low superatmospheric pressures may be employed in the coking ovens and when superatmospheric pressure is employed in this zone it may be substantially equalized or somewhat reduced in the succeeding fractionating, condensing and collecting portions of the system. The heating coil to which the relatively low-boiling oil is supplied may employ an outlet conversion temperature ranging, for example, from 900 to 1100° F. and a substantial superatmospheric pressure of from 200 to 1000 pounds, or thereabouts, per square inch is preferred at this point in the system although, when desired, lower pressures down to substantially atmospheric may be employed in this zone. The temperature prevailing in the coking chambers may range, for example, from 950 to 1200° F., or more.

As a specific example of one or the many possible operations of the invention, utilizing as raw charging stock a mixture of about two parts by weight of pulverized bituminous coal of high volatility and one part of coal tar; the high boiling reflux condensate is subjected, together with the raw charging stock, to a temperature of about 850° F. at the outlet from the heating coil at a superatmospheric pressure of about 200 pounds per square inch, low boiling fractions of the reflux condensate are separately subjected to a conversion temperature of approximately 950° F. at a superatmospheric pressure of about 350 pounds per square inch and are introduced into the coking ovens above the deposit of coke being accumulated therein. A temperature of about 1000° F. and substantially atmospheric pressure is employed in the coking ovens, the pressure being substantially equalized in the succeeding fractionating, condensing and collecting portions of the system. This operation may yield, per ton of charging stock, about 1250 pounds of coke of low volatility and about 45 gallons of high anti-knock motor fuel, the remainder, which comprises about 20% of the charging stock, being chargeable principally to gas which is of high calorific value and suitable for use as fuel.

I claim as my invention:

1. In a process for the treatment of finely divided non-asphaltic pyrobituminous material in admixture with hydrocarbon oil wherein the mixture is subjected to elevated temperature under non-coking conditions and introduced into a coking oven wherein vaporous products and non-vaporous residue are separated and the residue reduced to coke upon a highly heated refractory plate, heated from beneath by combustion of fuel, vaporous products from said coking oven subjected to fractionation, whereby their low boiling components, within the range of the desired final light distillate product of the process, are separated from their higher boiling components by condensation of the latter, said desirable low boiling vapors subjected to condensation and recovery, the improvement which comprises simultaneously subjecting a second hydrocarbon oil of lower boiling point than the first named oil to independently controlled conversion conditions of elevated temperature and introducing the resulting highly heated products into said coking oven to commingle with the vaporous products supplied therefrom to said fractionation and to supply additional heat to the upper surface of the material undergoing coking.

2. In a process for the treatment of finely divided non-asphaltic pyrobituminous material in admixture with hydrocarbon oil wherein the mixture is subjected to conversion temperature under non-coking conditions and discharged into a coking oven wherein vaporous products and non-vaporous residue are separated and the residue reduced to coke upon a highly heated refractory plate, heated from beneath by combustion of fuel, vaporous products from said coking oven subjected to fractionation, whereby their low boiling components, within the range of the desired final light distillate product of the process, are separated from their higher boiling components by condensation of the latter, said desirable low-boiling vapors subjected to condensation and recovery, the improvement which comprises simultaneously subjecting a second hydrocarbon oil of lower boiling point than the first-named oil to more severe conversion conditions of elevated temperature and introducing the resulting highly heated products into said coking zone to commingle with the vaporous products supplied therefrom to said fractionation and to supply additional heat to the upper surface of the material undergoing coking.

3. A process of the character defined in claim 1, wherein the second hydrocarbon oil subjected to said independently controlled conversion conditions comprises reflux condensate produced by said fractionation of the vaporous products from the coking oven.

4. A process of the character defined in claim 1, wherein the second hydrocarbon oil subjected to said independently controlled conversion conditions comprises hydrocarbon oil from an external source.

5. A process of the character defined in claim 1 wherein the second hydrocarbon oil subjected to said independently controlled conversion conditions comprises a mixture of hydrocarbon oil from an external source and reflux condensate produced by said fractionation of the vaporous products from the coking oven.

6. In a process for the pyrolytic conversion and coking of finely divided non-asphaltic pyrobituminous material in admixture with hydrocarbon oil wherein the mixture is subjected to mild conversion temperature at super-atmospheric pressure in a heating coil and introduced into a coking oven, wherein the vaporous products and non-vaporous residue are separated and the residue reduced to coke on a highly heated refractory plate, heated from beneath by combustion of fuel, the vaporous products from the coking oven subjected to fractionation, whereby their components boiling above the final light distillate product of the process are condensed as reflux condensate and the fractionated vapors of the desired end-boiling point condensed and recovered, the improvement which comprises simultaneously subjecting a hydrocarbon oil of lower boiling characteristics than the first-named oil to more severe conversion conditions of elevated temperature in a separate heating coil and introducing the resulting highly heated products into the coking oven to commingle with the vaporous products supplied from this zone to said fractionation and to heat the upper surface of the material undergoing coking.

7. A process of the character defined in claim 6, wherein tars and similar high coke-forming materials are separated from the vaporous products

from the coking oven and returned to the coking oven for further treatment while a substantial portion of the remaining components of the vapors condensed by said fractionation are subjected to further treatment in the first mentioned heating coil.

8. A process of the character defined in claim 6, wherein tars and similar high coke-forming materials are separated from the vaporous products from the coking oven and returned to the coking oven for further treatment while a substantial portion of the remaining components of the vapors condensed by said fractionation are returned to the last mentioned heating coil for further conversion.

9. A process of the character defined in claim 6 wherein the reflux condensate formed by said fractionation of the vaporous products from the coking oven is separated into low boiling and high boiling fractions and the low boiling fractions supplied to said separate heating coil for further conversion.

10. A process of the character defined in claim 6, wherein the reflux condensate formed by said fractionation of the vaporous products from the coking oven is separated into low boiling and high boiling fractions, the low boiling fractions supplied to said separate heating coil for further conversion and the high boiling fractions subjected to further treatment in the first mentioned heating coil.

11. A process of the character defined in claim 6, wherein the reflux condensate formed by said fractionation of the vaporous products from the coking oven is separated into low boiling and high boiling fractions and the high boiling fractions subjected to further treatment in the first mentioned heating coil.

12. A process of the character defined in claim 6, wherein the reflux condensate formed by said fractionation of the vaporous products from the coking oven is separated into low boiling and high boiling fractions and the low boiling fractions supplied to said separate heating coil for further conversion, together with low boiling hydrocarbon oil from an external source.

13. A process of the character defined in claim 6, wherein tars and similar high coke-forming materials are separated from the vaporous products from the coking oven and returned to the coking oven for further treatment, the remaining components of the vapors, boiling above the range of the desired final light distillate product of the process, which are condensed as reflux condensate, are separated into low boiling and high boiling fractions, the high boiling fractions subjected to further conversion in the first mentioned heating coil and the low boiling fractions returned to the last mentioned heating coil for further conversion.

14. A process for coking heavy hydrocarbon material which comprises depositing the material to be coked upon a substantially horizontal refractory plate in a coking zone, heating said plate from below by combustion of fuel and supplying a coking heat therethrough to the material to be coked, passing a hydrocarbon oil of lower boiling point than said heavy material in a restricted stream through a heating zone and heating the same therein to its cracking temperature, and discharging the thus heated light oil directly onto the material deposited on said plate to supply additional heat for the coking from above.

15. A combined coking and cracking process which comprises preheating heavy hydrocarbon oil in a heating zone under non-coking conditions, introducing the preheated oil into a coking zone and depositing residual portions thereof upon a substantially horizontal refractory plate in the coking zone, heating said plate from below by combustion of fuel and supplying a coking heat therethrough to the material deposited on the plate, passing a second hydrocarbon oil of lower boiling point than the first-named oil through a second heating zone and heating the same therein to its cracking temperature, and discharging the thus heated second oil directly onto the material deposited on said plate to supply additional heat for the coking from above.

16. A combined coking and cracking process which comprises depositing solid, non-asphaltic pyrobituminous material to be coked upon a substantially horizontal refractory plate in a coking zone, heating said plate from below by combustion of fuel and supplying a coking heat therethrough to the material to be coked, passing a hydrocarbon oil in a restricted stream through a heating zone and heating the same therein to its cracking temperature, and discharging the thus heated oil directly onto the material deposited on said plate to supply additional heat for the coking from above.

JOSEPH G. ALTHER.