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CONVERSION AND COKING OF HYDROCARBON OILS

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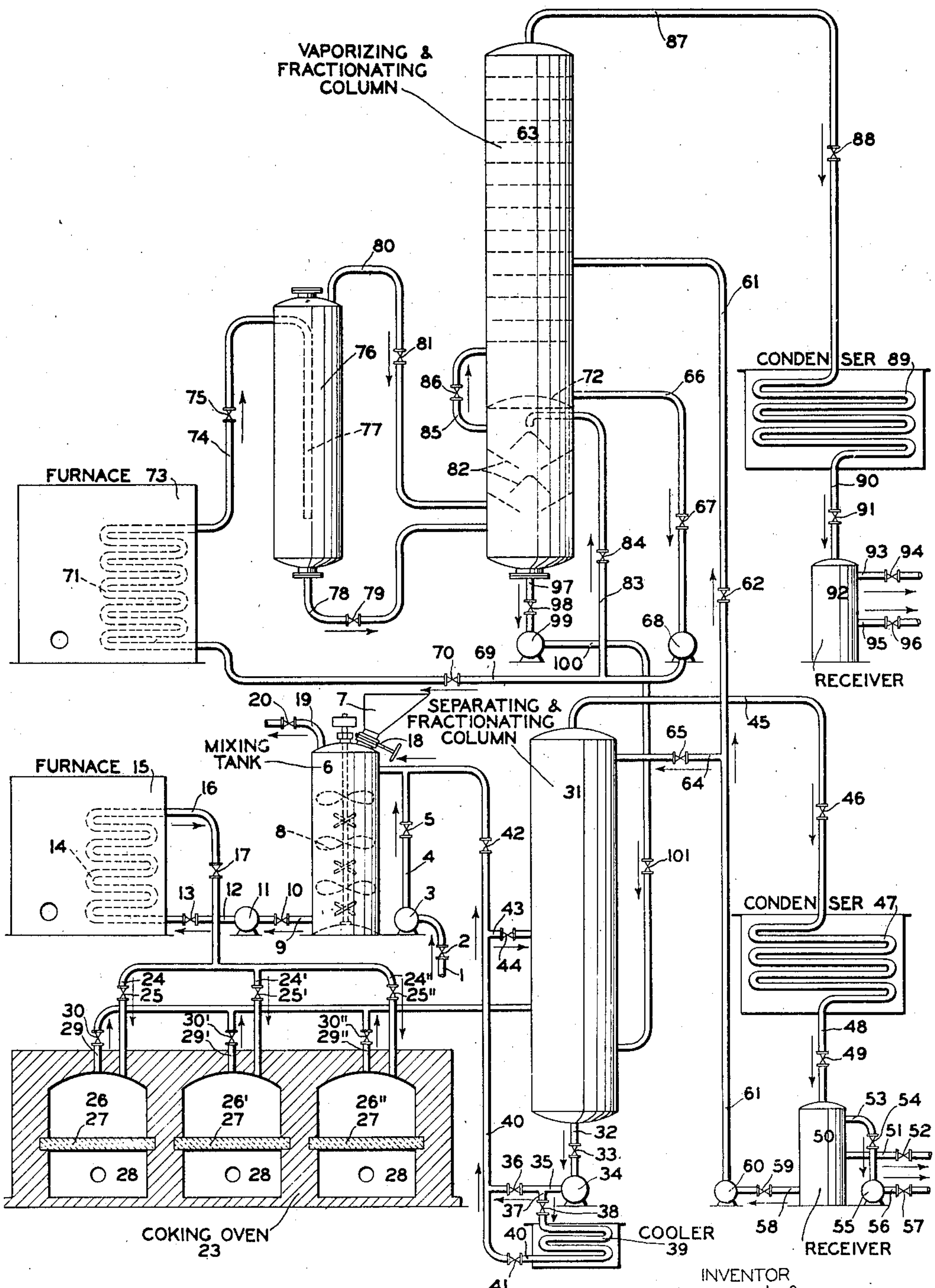

INVENTOR

ALFRED FISHER

BY Leo J. Gary

ATTORNEY

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CONVERSION AND COKING OF HYDROCARBON OILS

Alfred Fisher, Chicago, Ill., assignor to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

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2 Claims. (Cl. 196—56)

This invention particularly refers to an improved process and apparatus for the conversion and coking of mixtures of hydrocarbon oil and finely divided solid or semi-solid carbonaceous material, such as coal, peat, lignite, oil shale and the like, for the production, primarily, of low volatile coke and a light liquid product such as motor fuel of high anti-knock value, various intermediate products of the process being subjected to selected further conversion in the same system. The preferred charging stock for the process is a mixture of hydrocarbon oil and coal.

One specific embodiment of the present invention may comprise subjecting a mixture of hydrocarbon oil and finely divided carbonaceous material to mild conversion in a heating coil under non-coking conditions, introducing the heated material into a plurality of alternately operated coking ovens, preferably operated at slight subatmospheric pressure, wherein the residual conversion products are reduced to coke and the coke is substantially devolatilized by introducing the heated mixture onto highly heated surfaces upon which the coke is allowed to accumulate in a relatively thin layer, supplying the vaporous products from the coking ovens to a separating and fractionating column, also preferably operated at sub-atmospheric pressure, wherein their high-boiling components, including tars and similar high coke-forming materials, are separated from their lower boiling components suitable as light cracking stock, subjecting the latter, or all but their low-boiling components satisfactory as motor fuel, to conversion temperature at superatmospheric pressure in a heating coil and communicating reaction chamber, introducing the resulting vaporous and liquid conversion products into a reduced pressure vaporizing and fractionating column wherein the liquid products are subjected to further vaporization, the residual liquid separated from the vaporous products and the latter subjected to fractionation, whereby their components boiling above the range of the desired motor fuel 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, returning the reflux condensate to further conversion in the last mentioned heating coil, returning said residual liquid to the first mentioned separating and fractionating column for further vaporization at said subatmospheric pressure and commingling unvaporized residue therefrom with the charging stock mixture supplied to the first mentioned heating coil.

The preferred method of operation of the process of the present invention will be more apparent with reference to the accompanying diagrammatic drawing and the following description thereof. The drawing illustrates one specific form of apparatus embodying the features of the present invention, although the invention is not limited to use in the specific form of apparatus illustrated.

Referring to the drawing, raw oil charging stock, comprising any desired hydrocarbon oil such as crude petroleum, petroleum residue, fuel oil or the like, including such oils as coal tar, pitches and other heavy oils, is supplied through line 1 and valve 2 to pump 3, by means of which it is fed through line 4 and valve 5 into mixing tank 6 wherein it may be commingled and intimately mixed with other ingredients of the combined feed for the process. Coal or other suitable solid or semi-solid carbonaceous material is added to the mixing tank, preferably in finely divided form and in regulated amounts relative to the raw oil, through a hopper or other suitable charging device 7 of any suitable form. Mixing tank 6 is preferably equipped with a stirring device 8 of any desired type by means of which the carbonaceous material is finely dispersed throughout the body of the oil and the ingredients of the combined feed are maintained in a thoroughly commingled state. Other oils from within the system may be added to the materials in the mixing tank to make up the total combined feed for the process, as will be later more fully described, and the commingled materials are withdrawn from the mixing tank through line 9 and valve 10 to pump 11 by means of which they are fed through line 12 and valve 13 to heating coil 14.

When the charging stock is of a heavy viscous nature it may be necessary to heat the liquid charging stock and/or the combined feed by means of steam jacketed lines or a steam jacketed mixing tank or in any other suitable well known manner, not illustrated in the drawing, in order to facilitate the handling of this material. When desired, heat for this purpose may be recovered from within the system by means of heat exchangers or the like, not illustrated in the drawing. When mixing tank 6 is heated or when heated oil is supplied thereto a superatmospheric pressure may be maintained therein in order to minimize vaporization in this zone, in which case a suitable valve 18 may be provided beneath hopper 7 and the tank is also provided with a vent 19 controlled by valve 20 through which any incidental vapors evolved from the hot material in the mixing tank may pass to either fractionator of the system or elsewhere, as desired.

Heating coil 14 is located within a furnace 15 of any suitable form by means of which the combined feed passing therethrough is preferably heated quickly to the desired conversion temperature, preferably at a substantial superatmospheric pressure, without allowing sufficient conversion time in the heating coil to cause any detrimental formation and deposition of coke in this zone; a high rate of heating being maintained in furnace 15 and a high oil velocity being maintained through heating coil 14 for this purpose. The heated materials may pass from heating coil 14 through line 16 and valve 17 and are introduced into the coking oven 23, through lines 24, 24' and 24'', controlled by the respective valves 25, 25' and 25''.

Coking oven 23 preferably comprises a plurality of coking chambers 26, 26' and 26'' which may be alternately operated, cleaned and prepared for further operation in order to render the process continuous. It will be understood that any number of similar coking chambers may be employed, although only three are illustrated in the drawing. Each of the coking chambers has a floor 27, preferably constructed of suitable refractory high heat conductive material such as silicon carbide, fused aluminum oxide, aluminum silicate, fire clay or fire brick and the like, heated to a high temperature from beneath by means of the combustion of any suitable type of fuel in combustion zones 28. The heated oil from heating coil 14 is directed onto the highly heated floor of one or more of the coking chambers whereby the oil is coked and the coke is allowed to accumulate in a relatively thin layer to a depth of approximately 6 inches, more or less, over the highly heated floor. Following the coking operation, heating may be continued for a time, when desired, in order to devolatilize the coke to the desired degree, during which the oil to be coked is diverted to another coking chamber, and finally the layer of devolatilized coke is removed, by means of an hydraulic ram or in any other suitable well known manner, following which the chamber is prepared for further operation. Vaporous products are withdrawn from the coking chambers through lines 29, 29' and 29'' controlled by valves 30, 30' and 30'', respectively, and pass into fractionator 31 which, in the case here illustrated, also serves as a vaporizing and tar separating zone.

The vaporous products supplied to column 31 are separated in this zone into high-boiling components, including any tars or similar high coke-forming materials carried over with the vapors from the coking zone, and lower boiling components, including any materials within the boiling range of motor fuel as well as higher boiling components of the vapors suitable as light cracking stock, including, for example, materials within the boiling range of gas oil.

The high-boiling fractions which remain unvaporized or are condensed as reflux condensate in column 31 may collect within its lower portion to be withdrawn therefrom through line 32 and valve 33 to pump 34 by means of which they may be returned through line 35, valve 36, line 40 and valve 42 to mixing tank 6 to commingle therein with other ingredients of the charging stock mixture supplied to heating coil 14, as already described. When desired, a regulated portion of the high-boiling oils removed from the lower portion of column 31 may be returned to this zone, for example, by means of line 43 and valve 44 to serve as a refluxing medium in the lower portion of the column, in which case this material may be cooled to the desired degree by diverting the same from line 35 through line 37, valve 38, cooler 39, line 40 and valve 41. It may also be desirable to cool this material, prior to its introduction into mixing tank 6 in order to minimize vaporization in this zone, although it is also entirely within the scope of the present invention to supply the heated oil from the lower portion of column 31 direct to heating coil 14 by well known means, not shown in the drawing, without passing the same through the mixing tank.

Fractionated vapors of the desired end-boiling point, comprising said low-boiling components of the material supplied to column 31, pass from the upper portion of this zone through line 45 and valve 46 to condensation and cooling in condenser 47. The resulting distillate and uncondensable gas passes through line 48 and valve 49 to collection and separation in receiver 50. When desired, a regulated portion of the distillate may be withdrawn from this zone to storage or to any desired further treatment through line 51 and valve 52. Preferably, however, all or at least a portion of this material is subjected to further treatment in the same system, as will be presently described.

Preferably, as already indicated, a slight subatmospheric pressure is employed in the coking zone and in column 31 and, in order to avoid pumping of the hot vapors and gases from column 31, so as to maintain partial vacuum in these zones, condenser 47 and receiver 50 may also be maintained at subatmospheric pressure, the pressure being regulated by the removal of uncondensable gas from receiver 50 through line 53 and valve 54 to pump or compressor 55, from which the gas is discharged to storage or elsewhere, as desired, through line 56 and valve 57.

A regulated portion or all of the distillate collected in receiver 50 may be withdrawn therefrom through line 58 and valve 59 to pump 60 by means of which it is fed through line 61 and valve 62 into column 63. When desired, a regulated portion of this material may be diverted from line 61 through line 64 and valve 65 into the upper portion of column 31 to serve as a cooling and refluxing medium in this zone, regulating the vapor outlet temperature from column 31 and thus controlling the end-boiling point of the distillate from this zone. It is, of course, within the scope of the present invention to supply fractionated vapors from the upper portion of column 31 direct to column 63. This may be accomplished, for example, by means of a suitable pump or compressor, and required connecting lines, not illustrated, although in case this method of operation is employed, column 63 may, when desired, also be operated at sub-atmospheric pressure in order to obviate the use of a vacuum pump or compressor for the hot vapors; the vacuum pump in such cases being located in the gas release line from receiver 92. The distillate supplied to column 63, when this method of operation is employed, serves as a cooling and refluxing medium in this zone to assist fractionation of the vaporous conversion products supplied thereto, as will be later more fully described. When the distillate from receiver 50 contains an appreciable quantity of materials within the boiling range of the desired final motor fuel product of the process but of inferior motor fuel characteristics, particularly with respect to their anti-knock value, the distillate from receiver 50, instead of being supplied to column 63 may be supplied, by well known means, not illustrated, direct to heating coil 71 for further conversion in order to subject the inferior motor fuel components to conditions which will effect a substantial improvement in their anti-knock value.

The upper portion of column 63 serves as a fractionating zone for the vaporous conversion products supplied thereto, as will be later described, as well as distillate from receiver 50 supplied to this zone and subjected to vaporization therein. Reflux condensate resulting from said fractionation, including components of both the vaporous conversion products and any distillate from receiver 50 supplied to column 63, boiling above the range of the final light motor fuel product of the process, may collect upon a suitable partition or deck 72, to be withdrawn therefrom through line 66 and valve 67 to pump 68, by means of which it is supplied through line 69 and valve 70 to further conversion in heating coil 71.

A furnace 73 supplies the required heat to the oil passing through heating coil 71 to bring it to the desired conversion temperature, preferably at a substantial superatmospheric pressure, and the heated oil is discharged through line 74 and valve 75 into reaction chamber 76.

Chamber 76 is preferably also maintained at a substantial superatmospheric pressure, which may be either equalized or somewhat reduced relative to the pressure employed at the outlet from heating coil 71, and, although not illustrated, chamber 76 is preferably well insulated in order to conserve heat so that conversion of the heated materials supplied to this zone and more particularly their vaporous components, may continue therein. Any desired type of reaction chamber may be employed within the scope of the present invention. In the particular case here illustrated, the heated products from heating coil 71 are discharged into the lower portion of chamber 76 through an extended transfer line 77. In this type of operation a major portion of the liquid conversion products quickly separates from the vaporous conversion products in the lower portion of the chamber and may be quickly removed therefrom without allowing the liquid to remain in the chamber for a sufficient length of time to effect any appreciable further conversion thereof, thus avoiding the possibility of coke formation and deposition in the reaction chamber, while the vaporous conversion products pass upward through the chamber and are subjected during their passage therethrough to appreciable continued conversion time. Liquid conversion products are withdrawn, in the case illustrated, from the lower portion of chamber 76 through line 78 and valve 79 and are introduced, preferably at substantially reduced pressure, into the lower portion of column 63. The vaporous conversion products are removed from the upper portion of chamber 76 through line 80 and valve 81 and may also be introduced into the lower portion of column 63 either alone, as illustrated, or together with the liquid conversion products from chamber 76, by well known means, not illustrated.

In the case here illustrated, the lower portion of column 63 comprises a vaporizing chamber wherein, by virtue of the reduced pressure employed in this zone relative to that in reaction chamber 76, the liquid conversion products are subjected to further vaporization. Rough fractionating means such as baffles, perforated pans and the like indicated at 82 are preferably employed in the upper portion of the vaporizing section of column 63 for the purpose of assisting in the removal of entrained heavy liquid conversion products from the evolved vapors, and as a special feature of the present invention, a regulated portion of the reflux condensate from the upper portion of column 63 may, when desired, be returned through line 83 and valve 84 to the vaporizing section of the column to flow over baffles 82, serving as a refluxing medium. Vaporous conversion products pass from the vaporizing section of column 63 through line 85 and valve 86 into the upper or fractionating portion of the column wherein their insufficiently converted components are condensed as reflux condensate and returned, as already described, to further conversion in heating coil 71.

Fractionated vapors of the desired end-boiling point pass, together with uncondensable gas, from the upper portion of column 63, through line 87 and valve 88 to be subjected to condensation and cooling in condenser 89. The resulting distillate and gas passes through line 90 and valve 91 to collection and separation in receiver 92. Uncondensable gas may be released from the receiver through line 93 and valve 94. The distillate may be withdrawn from this zone through line 95 and valve 96 to storage or to any desired further treatment. A regulated portion of the distillate from receiver 92 may, when desired, be recirculated by well known means, not shown in the drawing, to the upper portion of column 63 to serve as a cooling and refluxing medium in this zone, assisting fractionation of the vapors and maintaining the desired vapor outlet temperature from the fractionator.

Residual liquid conversion products remaining unvaporized in the lower portion of column 63 are withdrawn therefrom through line 97 and valve 98 to pump 99 by means of which they may be returned through line 100 and valve 101 to the lower portion of column 31 whereby they are subjected to further vaporization under the subatmospheric pressure employed in this zone, the evolved vapors being subjected to fractionation, together with the vaporous products from the coking zone, while the unvaporized components of the residual liquid are returned, by means already described, to mixing tank 6 to commingle with the other ingredients of the charging stock mixture supplied to heating coil 14. It is, of course, also within the scope of the present invention to return the unvaporized residual liquid from the lower portion of column 63 direct to mixing tank 6 or to heating coil 14, by well known means not illustrated, although it is preferably returned to column 31 in order that it may be subjected to further vaporization in this zone. Pump 99 may be by-passed by well known means not illustrated, when it is not required.

In an apparatus such as illustrated and above described, the preferred range of suitable operating conditions may be approximately as follows: the conversion temperature employed at the outlet from the heating coil to which the charging stock mixture is supplied may range, for example, from 800 to 900° F., and preferably a substantial superatmospheric pressure within the range of 100 to 500 pounds, or thereabouts, per square inch is employed at this point in the system. As previously indicated a slight subatmospheric pressure is preferred in the coking zone and in the succeeding separating and fractionating column. This pressure may range, for example, from a few ounces to several pounds sub-atmospheric pressure. Coking temperatures employed may range from 950 to 1200° F., or thereabouts, and the coke produced may be further heated, when desired, to a temperature up to 1600° F., or more, for the purpose of devolatilizing the same. The second heating coil of the system may utilize a conversion temperature measured at the outlet therefrom ranging, for example, from 900 to 1050° F., preferably with a substantial superatmospheric pressure of from 200 to 800 pounds, or more, per square inch at this point in the system. This pressure may be either substantially equalized or somewhat reduced in the succeeding reaction chamber and preferably a substantially reduced pressure relative to that employed in the reaction chamber is employed in the vaporizing chamber, ranging, for example, from 100 pounds, or thereabouts, per square inch to substantially atmospheric pressure. Pressures employed in the fractionating, condensing and collecting portions of the system may be either substantially equalized or somewhat reduced relative to the pressure employed in the succeeding portions of the system.

As a specific example of the results obtainable in an operation such as above described utilizing a charging stock comprising a mixture of about two parts by weight of pulverized coal of high volatility and one part of coal-tar, there may be produced, per ton of charging stock, about 1300 pounds of coke of low volatility and about 42 gallons of motor fuel of high anti-knock value, the remaining 20%, or thereabouts, based on the charging stock, being principally gas suitable for use as fuel. The yield of motor fuel may be increased and the yield of coke reduced by employing a greater proportion of liquid charging stock and higher yields of motor fuel with lower yields of coke are also ordinarily obtainable when petroleum oils are substituted for the coal-tar as charging stock.

This application is a continuation-in-part of my earlier applications Serial Nos. 674,001 and 674,002.

I claim as my invention:

1. A process which comprises coking a mixture of hydrocarbon oil and solid pyro-bituminous material in a coking zone, fractionating the resultant vapors to form a relatively heavy fraction and a lighter fraction, cracking the lighter fraction in an independent cracking zone and separating cracked products thereof into vapors and residual oil in a zone apart from said coking zone, supplying said heavy fraction and said residual oil to the coking operation to constitute at least a part of said hydrocarbon oil, fractionating the last-named vapors and returning resultant reflux condensate to the cracking zone, and finally condensing the fractionated vapors.

2. A process which comprises coking a mixture of hydrocarbon oil and solid pyro-bituminous material and introducing the resultant vapors to a separating zone, separating from the vapors in this zone heavy coke-forming constituents thereof and subsequently condensing the remaining vapors, cracking condensate formed by the last-named condensing step and separating cracked products thereof into vapors and unvaporized oil under a higher pressure than is maintained in said separating zone, discharging the unvaporized oil into the separating zone whereby vapors are evolved therefrom by the pressure reduction and the residual portion thereof commingled with said heavy constituents, and supplying the resultant heavy mixture formed in the separating zone to the coking operation.

ALFRED FISHER.