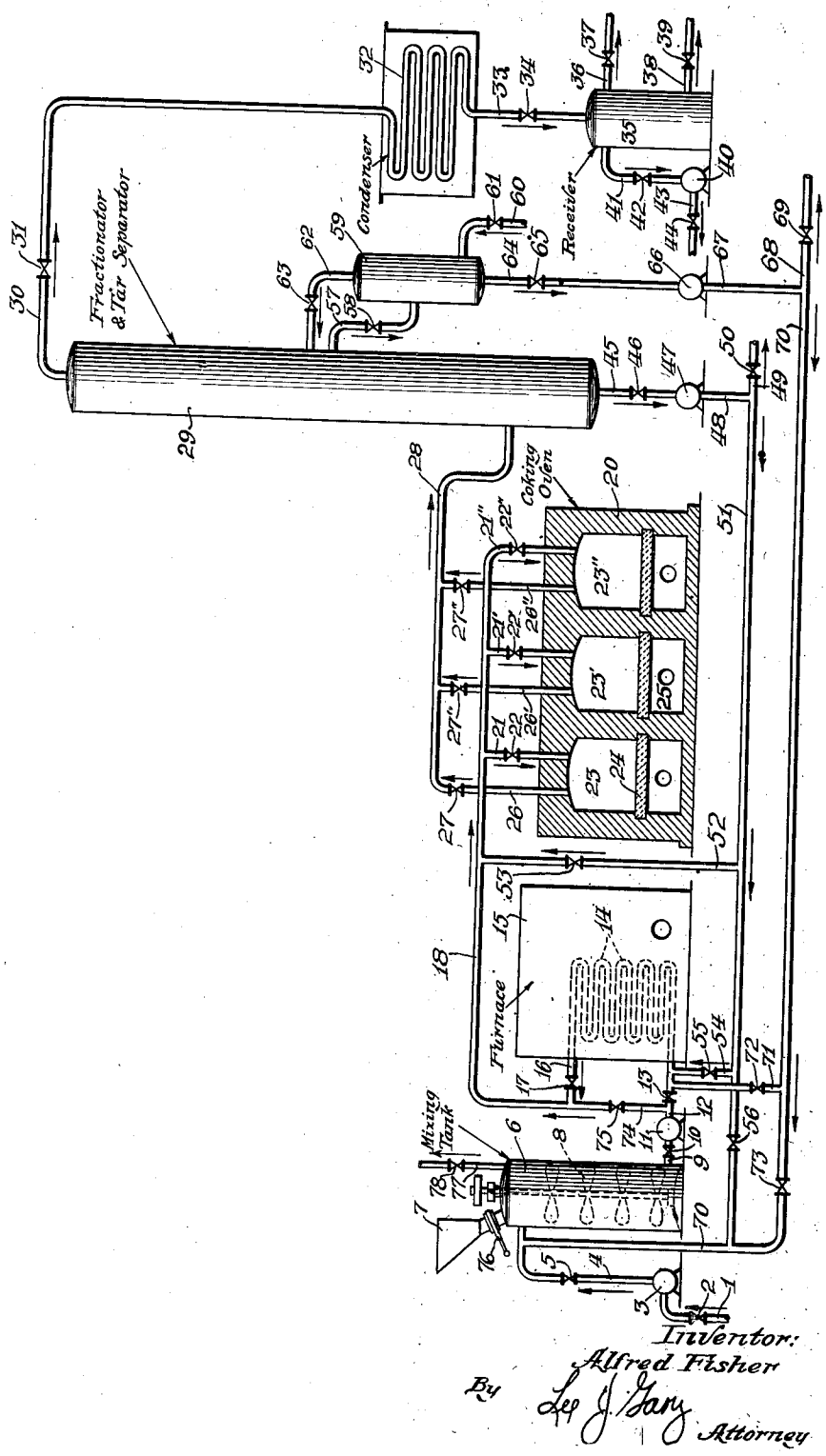
March 9, 1937. A. FISHER 2,073,367

CONVERSION AND COKING OF CARBONACEOUS MATERIALS.

Filed June 2, 1933



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Patented Mar. 9, 1937 2,073,367

UNITED STATES PATENT OFFICE

2,073,367

CONVERSION AND COKING OF CARBONACEOUS MATERIALS

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Application June 2, 1933, Serial No. 674,002

3 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 solid or semi-solid bituminous material, such as coal, peat, lignite, oil shale and the like, for the production of low volatile coke, gas, light distillate such as motor fuel, and intermediate liquid products, which latter may be subjected to further conversion in the same or a separate system or may be collected as a final product of the process. The preferred mixture to be treated is coal and oil.

In one embodiment the coking zone may comprise a plurality of alternately operated coking ovens of the type wherein the mixture of oil and bituminous material to be coked is first heated in a coil preferably to a mild cracking temperature but insufficient to cause objectionable coke depositions and the mixture is then introduced onto a highly heated surface, preferably of suitable heat-conductive refractory material such as silicon carbide, (e. g. carborundum) fused aluminum oxide, aluminum silicate, suitable fire clays or brick and the like, upon which the resulting coke is allowed to accumulate in a relatively thin layer, to be removed by means of an hydraulic ram, or in any other suitable well known manner, after the coke layer has been built up to the desired thickness. A coking zone of this character permits the use of higher temperatures than are ordinarily permissible in metal coking chambers without resorting to expensive steel alloys for the walls of the vessel. In ovens such as described above, the heat is applied directly to the under surface of the heat-conductive refractory material and is transmitted directly therethrough to the material undergoing coking and the bed of coke accumulated thereon. Coking zones of this character may be operated at subatmospheric, substantially atmospheric, or low superatmospheric pressure, are easily cleaned by the use of hydraulic rams in a manner similar to that employed in ordinary carbonizing retorts, and are easily adaptable to alternate operation, so that the duration of the operation of the process is not limited to the capacity of the coking retort.

One specific embodiment of the present invention may comprise subjecting a mixture of hydrocarbon oil and finely divided carbonaceous material to conversion in a heating coil under non-coking conditions, introducing the heated material into a plurality of alternately operated coking ovens, wherein the residual conversion products are reduced to coke and the coke is substantially devolatilized by introducing the mixture from the heating coil onto a highly heated refractory surface, withdrawing the vaporous products from the coking ovens, removing therefrom their high-boiling tar-like components and similar high coke-forming materials, subjecting the remaining vapors to further fractionation whereby their components of an intermediate nature, boiling above the range of the desired final light distillate product of the process and of lower boiling nature than said heavy tar-like and high coke-forming materials, are condensed as intermediate condensate, subjecting the fractionated vapors of the desired end boiling point to condensation, and collecting and separating the resulting distillate and gas. The tar-like and similar high coke-forming materials separated from the vaporous products from the coking ovens may, when desired, be withdrawn from the system to storage or to further treatment in another process, but preferably they are returned to further treatment in the same system by supplying them either direct to the coking ovens or to commingle with the charging stock mixture supplied to the heating coil. The intermediate condensate separately recovered from the vaporous products from the coking ovens may be withdrawn from the system to storage, or preferably it is returned to the heating coil for further conversion. This material ordinarily is ideal as clean cracking stock and may be supplied as such to the same or another process.

As a modification of the specific embodiment above described, it is also within the scope of the present invention to supply the intermediate condensate, or when desired, the total condensate recovered from the vaporous products from the coking ovens, to the heating coil of the system for conversion, introducing the heated products therefrom into the coking ovens, in which case preferably all or a portion of the charging stock mixture comprising hydrocarbon oil and finely divided solid or semi-solid carbonaceous material may be supplied direct to the coking ovens without passing through the heating coil. This latter type of operation permits the use of more severe conversion conditions in the heating coil, particularly when only the intermediate condensate is supplied to this zone, and may result in the production of increased quantities of motor fuel of higher anti-knock value.

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

accomplished. The drawing and the following description thereof will serve to more clearly explain the various modifications of the operation of the process, which however, are not to be considered equivalent but may be selected to suit the particular requirements of the material undergoing treatment and to accomplish the desired results.

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 is 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 suitable form, 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 may be 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 means (not shown) 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 shown).

Heating coil 14 is located within a furnace 15 of any suitable form, by means of which the charging material supplied thereto is heated to the desired conversion temperature, preferably at a substantial superatmospheric pressure. When heavy oils and solid or semi-solid carbonaceous material are passed through the heating coil as already indicated, the size of the heating coil, the velocity of the materials passing therethrough and the rate of heating are preferably such that the desired conversion temperature is reached without allowing sufficient time in the heating coil to cause any detrimental formation and deposition of coke in this zone, a high rate of heating preferably being employed in the furnace and a high oil velocity being maintained in the heating coil for this purpose. The heated materials pass from heating coil 14 through line 16, valve 17 and line 18, and are introduced into coking oven 20 through lines 21, 21' and 21'', controlled by the respective valves 22, 22' and 22''.

Coking oven 20 preferably comprises a plurality of coking chambers such as 23, 23' and 23'', 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 24, preferably constructed of suitable refractory highly heat-conductive material such as silicon carbide, fused aluminum oxide, aluminum silicate and the like, heated to a high temperature from beneath by means of the combustion of any suitable type of fuel in combustion zones 25. The heated products from heating coil 14 are introduced 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 which heating may be continued for a time in order to devolatilize the coke to the desired degree, during which the oil is diverted to another coking chamber, and finally the layer of devolatilized coke is removed by means of an hydraulic ram or 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 26, 26' and 26'', controlled by valves 27, 27' and 27'', respectively, and pass through line 28 into a fractionator and tar separator 29, in the lower portion of which their heavy components of high coke-forming characteristics, such as tars and the like, are removed from their lower boiling components, which latter are further fractionated for the separation and removal of intermediate condensates boiling above the range of the desired final light distillate product of the process and of lower boiling characteristics than said heavy high coke-forming materials.

Fractionated vapors of the desired end boiling point are passed, together with gas produced by the operation, from the upper portion of fractionator 29 through line 30 and valve 31 to be subjected to condensation and cooling in condenser 32. The resulting distillate and gas pass through line 33 and valve 34 to collection and separation in receiver 35. Gas may be released from the receiver through line 36 and valve 37. The distillate may be withdrawn from this zone through line 38 and valve 39 to storage or to any desired further treatment. When desired, a portion of the distillate collecting in receiver 35 may be returned by well known means not shown in the drawing to the upper portion of fractionator 29, serving as cooling and refluxing medium in this zone to assist fractionation of the vapors and maintain the desired vapor outlet temperature from the fractionator, thus controlling the end boiling point of the final light distillate product of the process.

In the preferred operation of the process sub-atmospheric pressures or vacuum are employed in the coking chambers and, in order to avoid passing the hot vaporous products from the coking oven through a vacuum pump or compressor, sub-atmospheric conditions are also preferably maintained in the succeeding fractionating, condensing and collecting portions of the system. A pump or compressor 40 may be provided, as illustrated in the drawing, for the purpose of withdrawing gases from receiver 35 through line 41 and valve 42, discharging the same through line 43 and valve 44 to a gas-holder, or elsewhere as desired, for the purpose of maintaining the desired sub-atmospheric pressure in the coking oven and succeeding portions of the system.

High boiling oils, tars and the like of high boiling and easy coking characteristics separated from the vaporous products from the coking oven in the fractionator and tar separator 29 are

withdrawn from the lower portion of this zone through line 45 and valve 46 to pump 47, from which they are passed through line 48 and may be discharged, all or in part, from the system through line 49 and valve 50, to storage or further treatment outside of the system, as desired. Preferably, however, a regulated portion or all of this material passes from line 48 through line 51 and may be returned by means of line 52, valve 53, line 13 and lines 21, 21' and 21'', through the respective valves 22, 22' and 22'', into the coking chambers for further treatment and reduction to coke or, when desired, this material may be returned to further conversion in heating coil 14 by passing the same from line 51 through line 54, valve 55 and line 12 directly into heating coil 14, or by passing it through valve 56 in line 51 and through line 70 into mixing tank 6 to commingle with the charging stock mixture subsequently supplied to the heating coil.

Intermediate condensates recovered from the vaporous products undergoing fractionation may be withdrawn as one or a plurality of side streams from fractionator 29, for example, through line 57 and valve 58 to column 59, wherein they may be reboiled by means of steam introduced through line 60 and valve 61, or in any other suitable well known manner to vaporize any components within the boiling range of the desired final light distillate product of the process and to free the oil of any entrained gases. The vapors evolved by reboiling the intermediate condensates may be returned to fractionator 29 through line 62 and valve 63. The reboiled intermediate condensates may pass from column 59 through line 64 and valve 65 to pump 66. It will be understood that such reboiling of the intermediate products is not essential to the operation of the process and may be omitted when desired. The intermediate condensate passes from pump 66 through line 67 to the heating coil for further conversion, or it may be discharged from the system to storage, or to conversion in another cracking system or elsewhere as desired through line 68 and valve 69. When the intermediate condensate is returned to further conversion in heating coil 14, it is passed through lines 67, 70, 71, valve 72 and line 12 direct to heating coil 14, or may pass through valve 73 in line 70 into mixing tank 6 to commingle therein with the other ingredients of the combined feed supplied to heating coil 14.

When liquids are supplied from within the system, as already described, to mixing tank 6 they may, when desired, be cooled by well known means, not shown in the drawing, prior to their introduction into this zone. However, when it is desired to conserve the heat remaining in these products and in case it is not desirable to supply them direct to heating coil 14, as has been previously described, or when the charging stock is preheated, prior to its introduction into the mixing tank, or when heat is supplied to the mixing tank by means of a steam coil or steam jacket or the like, mixing tank 6 may be operated at substantial superatmospheric pressure in order to minimize vaporization in this zone and is preferably well insulated to conserve heat. In case the mixing tank is operated at superatmospheric pressure a suitable valve 76 may be provided beneath hopper 7 and the tank is preferably provided with a vent 77 controlled by valve 78 through which any incidental vapors evolved from the hot materials in the mixing tank may pass to the fractionator or elsewhere, as desired.

As a modification of the operation above described, intermediate condensates from fractionator 29 may comprise the only oil supplied to heating coil 14, in which case the charging stock mixture, including when desired, high boiling oils removed from the lower portion of fractionator 29, as already described, may be diverted from heating coil 14 and passed from line 12 through line 74, valve 75 and line 18 to the coking oven, commingling in line 18 with the heated intermediate condensates from heating coil 14, which are also discharged into the coking oven. It will be understood that, if desired, the heated oil from heating coil 14 and the charging stock mixture may be separately introduced into the coking oven by well known means not shown in the drawing instead of commingling in line 18 as illustrated.

When the charging stock mixture is supplied to the heating coil a conversion temperature measured at the outlet from this zone within the range of 850 to 900° F., is preferably employed, and preferably a substantial superatmospheric pressure is employed in the heating coil, ranging for example from 100 to 500 pounds, or thereabouts, per square inch measured at the outlet therefrom. A substantially reduced pressure is preferably employed in the coking chambers, sub-atmospheric pressure being preferred in the coking zone, although when desired substantially atmospheric or superatmospheric pressure may be employed in this zone. The pressure employed in the coking zone may be substantially equalized in the succeeding fractionating, condensing and collecting portions of the system. When only intermediate condensates from the fractionator are supplied to the heating coil more severe conversion conditions are preferred in this zone, the temperature at the outlet therefrom ranging for example, from 925 to 1050° F., or thereabouts, preferably with a substantial superatmospheric pressure at the outlet from the heating coil of from 200 to 800 pounds or more per square inch. The temperature at which the materials to be coked are heated in the coking ovens may range, for example, from 900 to 1200° F., or more, and when desired the coke accumulated therein may be further devolatilized by employing temperatures as high as 1600° F., or more in the coking oven after the mixture of materials to be coked has been diverted therefrom, the coking oven being isolated when desired from the rest of the system during the devolatilizing operation.

As a specific example of the operation of the invention, the charging stock is a mixture of about equal parts by weight of pulverized high volatile bituminous coal and coal tar. The total combined feed supplied to the heating coil comprises the charging stock mixture, the heavy high coke-forming oils and the intermediate condensate removed from the fractionator and tar separator. The combined feed is subjected in the heating coil to an outlet temperature of approximately 900° F., at a superatmospheric pressure of about 200 pounds per square inch and is introduced into the coking ovens, which are operated at a substantial sub-atmospheric pressure and wherein the non-vaporous conversion products are reduced to coke at a temperature of approximately 1150° F. The accumulated coke may be further devolatilized at a temperature of approximately 1500° F.

An overhead product comprising motor fuel of about 400° F., end boiling point is recovered from

the fractionator. This operation will produce, per ton of raw charging stock, about 1200 pounds of low volatile coke, approximately 55 gallons of motor fuel of good anti-knock value, and about 20% by weight of gas suitable for use as fuel. The use of a fuel oil from petroleum as a carrier for the coal will increase the yield of motor fuel and decrease the yield of coke and gas.

The conditions of operation and results shown are illustrative only and are not to be considered as limitations, as these may be varied widely without departing from the broad spirit and scope of the invention.

I claim as my invention:

1. A process for the pyrolytic conversion and coking of finely divided solid bituminous material and hydrocarbon oil which comprises adding the solid material to the oil, subjecting the mixture to conversion temperature under substantially non-coking conditions, introducing the heated products into a coking zone wherein the residue is coked in a relatively thin layer upon a highly heated surface, subjecting the vaporous products from the coking zone to fractionation, whereby their components boiling above the range of the desired final light distillate product of the process are condensed and separated into selected low-boiling and higher boiling fractions, subjecting fractionated vapors of the desired end-boiling point to condensation, collecting and separating the resulting distillate and gas and returning the selected low-boiling fractions of the condensate resulting from said fractionation of the vaporous products to further conversion with the charging stock mixture and returning said higher boiling fractions for further treatment direct to the coking zone.

2. A process for the pyrolytic conversion and coking of finely divided solid bituminous material and hydrocarbon oil which comprises adding the solid material to the oil, introducing the mixture into a coking zone wherein the volatiles of the mixture are substantially vaporized and the residue is reduced to coke in a relatively thin layer upon a highly heated surface, subjecting the vaporous products from the coking zone to fractionation whereby their components boiling above the range of the desired final light distillate product of the process are condensed and separated into low-boiling and higher boiling fractions, subjecting fractionated vapors of the desired end-boiling point to condensation, collecting and separating the resulting distillate and gas, returning said higher boiling fractions for further treatment direct to the coking zone, subjecting said low-boiling fractions of the condensate recovered by fractionation of the vapors to pyrolytic conversion under independently controlled conditions of elevated temperature and superatmosphere pressure and introducing the resulting products into the coking zone.

3. A process for the pyrolytic conversion and coking of finely divided solid bituminous material and hydrocarbon oil which comprises adding the solid material to the hydrocarbon oil, subjecting the mixture to conversion temperature under substantially non-coking conditions, introducing the heated products into a coking zone wherein the residue is coked, subjecting the vaporous products from the coking zone to fractionation, whereby their components boiling above the range of the desired final light distillate product of the process are condensed and separated into selected low-boiling and higher boiling fractions, subjecting fractionated vapors of the desired end-boiling point to condensation, collecting and separating the resulting distillate and gas and returning the selected low-boiling fractions of the condensate resulting from said fractionation of the vaporous products to further conversion with the charging stock mixture and returning said higher boiling fractions for further treatment direct to the coking zone.

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