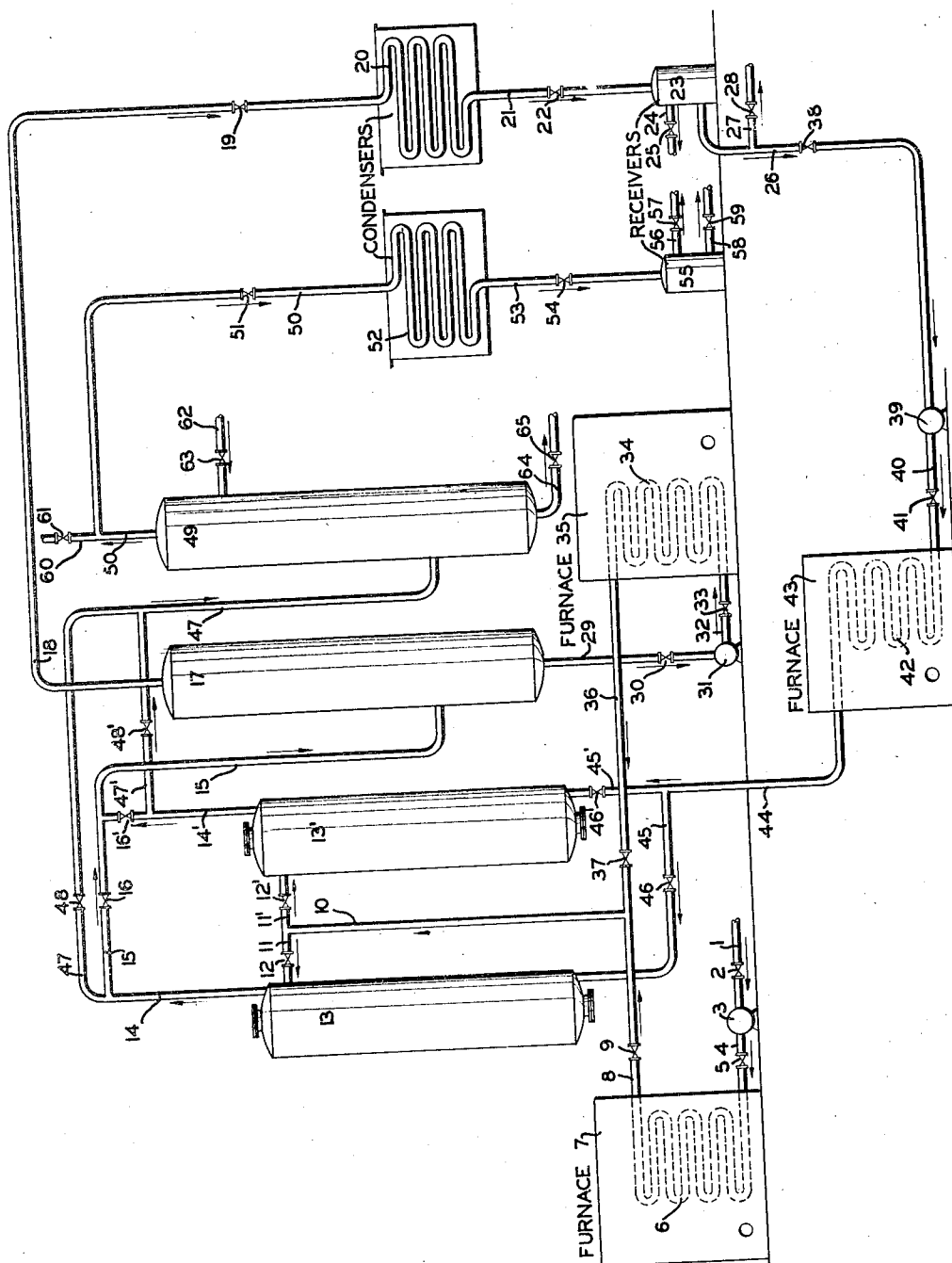


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TREATMENT OF HYDROCARBONS

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This invention relates to the treatment of liquid and solid hydrocarbonaceous materials and more particularly refers to an improved process and apparatus for the conversion and coking of a mixture of hydrocarbon oil and solid bituminous or hydrocarbonaceous material accompanied by substantial devolatilization of the carbonaceous residue.

Suitable charging stocks for the process of the present invention comprises any hydrocarbon oil ranging from relatively light distillates such as gasoline, kerosene, naphthas, etc. to heavy residual oils, asphalts, pitches and the like containing appreciable quantities of solid bituminous or hydrocarbonaceous material which has been added thereto or which the oil contains in its natural state. When solid hydrocarbonaceous material such as coal or coal wastes, peat, lignite, natural or synthetic asphaltic materials and the like are added to the oil they are preferably added in pulverized or colloidal form in such a manner and in such quantities that no objectionable amount of solid material will separate from the mixture and be deposited during passage thereof through the heating element, through which the charging stock is fed prior to its introduction into the coking zone.

The process is preferably operated for the production of maximum yields of light distillate products, such as motor fuel of high antiknock value, together with the production of a carbonaceous residual product of low volatile content. However, when desired, the process may be operated for the production of high yields of gas at the expense or even to the exclusion of light distillate products.

The primary principles of the present invention comprise subjecting charging stock, comprising liquid and solid hydrocarbonaceous material, and intermediate liquid products of the operation to conversion and coking, periodically isolating the coke thus produced from the cracking and coking cycle and subjecting it to devolatilization by passing therethrough distillate produced by the cracking and coking operation reheated to a relatively high temperature.

A more specific embodiment of the invention may comprise subjecting charging stock comprising a mixture of hydrocarbon oil and coal to heating in a heating element, introducing the heated materials into an enlarged coking zone, subjecting vapors from the coking zone to fractionation, condensing and collecting a relatively light distillate product resulting from said fractionation, subjecting reflux condensate resulting

from said fractionation to independently controlled conversion conditions in a separate heating element and introducing the heated material into said coking zone, periodically isolating said coking zone from the operating cycle described and accomplishing conversion and coking of the charging stock and reflux condensate in an alternate coking zone, heating said relatively light distillate product resulting from the conversion and coking operation to a relatively high temperature in a separate heating element, introducing the heated material into the bed of coke in said isolated coking zone, separately fractionating the vapors therefrom and separately condensing and collecting the light distillate product.

The heating element through which the charging stock is passed, prior to its introduction into the coking zone, may employ relatively mild conversion conditions, or temperatures below the conversion range may be utilized in this zone. In any event the conditions employed in this zone preferably are sufficiently mild to preclude the deposition of any objectionable quantity of solid material in the heating element.

When the process is operated for the production of maximum yields of light distillate products, such as motor fuel of high antiknock value, temperature and pressure conditions employed in the heating element through which distillate from the cracking and coking operation is passed are, preferably, not sufficiently severe to effect the production of undesirable quantities of gas and in the preferred embodiment of the invention are of a nature which will effect conversion of reforming of the distillate for the production of maximum yields of material of motor fuel boiling range having high antiknock characteristics. However, when the production of high yields of gas is desired more severe conversion conditions may be employed in this zone and in all cases the heated distillate is introduced into the bed of coke at a temperature sufficient to effect substantial devolatilization thereof.

Reflux condensate produced by fractionation of the vapors evolved in the devolatilizing operation may be returned to any or in part, to all the three heating elements of the system or may be withdrawn, all or in part, from the system. Distillate resulting from the devolatilizing operation comprises the final light distillate product of the system when such is produced but may, when desired, and especially when the process is operated for the production of high

yields of gas, be returned to the heating element to which distillate from the conversion and coking operation is supplied.

The attached diagrammatic drawing illustrates one specific form of apparatus embodying the principles of the present invention and the following description of the drawing will serve to more clearly illustrate the process of the invention as it may be practiced in the apparatus shown.

Charging stock for the system may be supplied through line 1 and valve 2 to pump 3 from which it is fed through line 4 and valve 5 to heating element 6. Heating element 6 is located in a furnace 7 of any suitable form and the material supplied thereto is heated to the desired temperature under any desired pressure conditions and passes therefrom through line 8, valve 9, lines 10 and 11 and valve 12 into chamber 13.

Vapors from chamber 13 pass through lines 14 and 15 and through valve 16 to fractionation in fractionator 17 wherein the relatively heavy components are condensed as reflux condensate, collecting in the lower portion of the fractionator to be withdrawn therefrom to further treatment as will be later more fully described. Vapors from fractionator 17, comprising relatively light distillate and uncondensable gas, are withdrawn from the fractionator through line 18 and valve 19 to be subjected to condensation and cooling in condenser 20, the resulting distillate and uncondensable gas from which passes through line 21 and valve 22 to be collected in receiver 23. Gas may be released from receiver 23 through line 24 and valve 25 while distillate is withdrawn from this zone through line 26 to be subjected, all or in part, to further treatment, as will be later more fully described, or, when desired, a portion of the distillate may be withdrawn from the system through line 27 and valve 28.

Reflux condensate collecting within the lower portion of fractionator 17, as already described, is withdrawn therefrom through line 29 and valve 30 to pump 31, by means of which it is fed through line 32 and valve 33 to heating element 34. Heating element 34 is located in a furnace 35 of any suitable form and the oil supplied thereto is subjected to conversion under independently controlled temperature and pressure conditions, which are preferably more severe than the conditions employed in heating element 6. Heated products from heating element 34 pass through line 36 and valve 37 into line 10, commingling therein with the heated charging stock from heating element 6 and passing therewith through line 11 and valve 12 into chamber 13.

Chambers 13 and 13' comprise alternately operated coking and carbonizing zones, two or more of which may be utilized in the operation of the process. For example, when chamber 13 has become filled to the desired extent with coke, resulting from the conversion and coking operation, it is isolated from the conversion and coking portion of the system by closing valves 12 and 16, in lines 11 and 15 respectively, the heated materials from heating elements 6 and 34 being thence passed through line 11' and valve 12' into coking chamber 13'. Vapors from chamber 13' thence pass through line 14' and valve 16' into line 15 to be subjected thereafter to the treatment already described, to which vapors from chamber 13 have been subjected. Thus the continuity of the cracking and coking operation is maintained while the coke previously deposited in chamber 13 is subjected to devolatilization, as will be de-

scribed. It will be understood that any number of a plurality of coking and carbonizing zones may be utilized, for example, one or more such zones may be utilized for the cracking and coking operation while the coke deposited in one or more previously operated zones is being devolatilized and another or other such zones are being cleaned and prepared for the coking operation. Thus, after one or more chambers has been filled to the desired extent with coke, cracking, coking and carbonizing operations may be carried on simultaneously for an indefinite period.

After a substantial deposit of coke has been accumulated in chamber 13, for example, and this zone has been isolated from the cracking and coking cycle, distillate withdrawn from receiver 23 through line 26, as previously described, is supplied through valve 38 to pump 39 from which it is fed through line 40 and valve 41 to heating element 42. Heating element 42 is located in a furnace 43 of any suitable form and the distillate supplied thereto is heated to a relatively high temperature under any desired pressure conditions and is thence discharged, preferably without substantial loss of heat, through line 44, line 45 and valve 46 into the bed of coke in chamber 13, preferably being introduced into the lower portion of this zone in such a manner as to pass upward through substantially the entire mass of coke therein, whereby substantial devolatilization of the coke is accomplished. Vapors resulting from the devolatilizing or carbonizing operation pass from chamber 13 through line 14, line 47 and valve 48 to fractionation in fractionator 49. It will be understood that when chamber 13' is being utilized as the carbonizing zone the heated distillate from heating element 42 passes from line 44 through line 45' and valve 46' into coking chamber 13' and vapors from this zone pass through line 14', line 47' and valve 48' into line 47 and thence to fractionator 49.

The function of fractionator 49 will depend primarily upon the desired products for which the process is operated. When maximum quantities of light distillate such as motor fuel of high antiknock value are desired, fractionator 49 may function in much the same manner as fractionator 17, distillate and uncondensable gas being withdrawn through line 50 and valve 51, subjected to condensation and cooling in condenser 52 thereafter passing through line 53 and valve 54 to be collected in receiver 55, from which uncondensable gas may be released through line 56 and valve 57 while distillate is withdrawn through line 58 and valve 59. However, when the process is operated for the production of high yields of gas to the exclusion of light distillate products, fractionation may be so controlled in column 49 that substantially only uncondensable gas is withdrawn from the upper portion thereof, passing through line 60 and valve 61 to a gas holder or elsewhere, as desired. In the latter case column 49, may if desired, function as an absorber, absorber oil being introduced through line 62 and valve 63 while the enriched absorber oil is withdrawn from the lower portion of column 49 through line 64 and valve 65. When the liquid portion of the charging stock supplied to the process is of such a nature that it will function as a suitable absorber oil, all or a portion of it may be introduced into column 49, as described, in which case the enriched absorber oil is preferably directed to heating element 6 by well known

means, not illustrated in the drawing. When column 49 functions as a fractionator wherein the relatively heavy components of the vapors supplied thereto are condensed, collecting as reflux condensate in the lower portion of this zone, said reflux condensate may be withdrawn through line 64 and valve 65 and may be directed, all or in part, to storage or to any of the heating elements 6, 34 or 42 for further treatment or the reflux condensate may be treated in any combination of the manners described.

Pressures employed within the system may range from substantially atmospheric to super-atmospheric pressures as high as 2000 pounds, or more, per sq. in. Temperatures employed in the various heating elements may range from temperatures below the conversion range, of the order to 750° F. or less to gas-making temperatures of the order of 1800° F. or thereabouts. Temperatures employed in the heating element to which the charging stock is supplied may range from 750° F. or less to 900° F. or thereabouts. Substantial super-atmospheric pressures of the order of 100 to 500 pounds per sq. in. are preferably employed in this zone. The heating element to which reflux condensate from the fractionator of the conversion and coking system is supplied preferably utilizes temperatures of the order to 900 to 1050° F. with pressures ranging from 100 to 500 pounds or thereabouts per sq. in. Pressures employed in the chamber or chambers utilized as a reaction and coking zone preferably range from 100 to 500 pounds or thereabouts per sq. in. although lower pressures down to substantially atmospheric may be employed, when desired. Carbonization of the coked residue is preferably effected at substantially atmospheric or relatively low super-atmospheric pressure although, when desired, substantial super-atmospheric pressure up to 500 pounds or thereabouts per sq. in. may be employed in the carbonizing zone. When conversion or reforming of the distillate from the cracking and coking operation for the production of maximum yields of high antiknock motor fuel is desired this material, which serves as a heat carrying medium for the carbonizing operation, is preferably subjected, in the heating element, to temperatures of the order of 950 to 1050° F. under substantial super-atmospheric pressures ranging from 300 to 800 pounds or more per sq. in. When high yields of gas are desired the distillate may be subjected to higher temperatures ranging, for example, from 1000 to 1800° F. preferably under substantially atmospheric or relatively low super-atmospheric pressure.

As a specific example of the operation of the process of the present invention, the charging stock comprises a mixture of about equal parts by weight of mid-continent fuel oil of about 24° A. P. I. gravity and pulverized bituminous coal having a volatile content of approximately 38 percent. The coal-in-oil mixture is subjected in a heating element to a temperature of approximately 800° F. under a super-atmospheric pressure of approximately 200 pounds per sq. in. Reflux condensate from the fractionator of the conversion and coking portion of the system is subjected, in a separate heating element, to a temperature of about 950° F. under a super-atmospheric pressure of approximately 350 pounds per sq. in. The coking zone is operated under a pressure of approximately 200 pounds per sq. in., which pressure is substantially equalized in the succeeding fractionating, condensing and collect-

ing portions of the conversion and coking system. The coke produced during this portion of the operation may have a volatile content of approximately 15 percent and the distillate produced which may, for example, have an end boiling point of approximately 500° F., may have an antiknock value equivalent to an octane number of approximately 50. This portion of the operation may yield, per barrel of charging stock, approximately 170 pounds of coke, about 55 percent of light distillate and approximately 600 cubic feet of gas. When the coking zone has become substantially filled with coke it is isolated from the cracking and coking cycle, which is continued in an alternate coking zone. Distillate produced by the cracking and coking operation heated in a separate heating element to a temperature of approximately 1000° F. under a super-atmospheric pressure of about 800 pounds per sq. in., is thence introduced into the bed of coke in the chamber isolated from the cracking and coking cycle. The carbonizing zone is maintained under a super-atmospheric pressure of approximately 100 pounds per sq. in. Vapors from this zone are subjected to fractionation and the resulting light distillate, substantially corresponding in boiling range to motor fuel, is collected. By the latter steps of the process the volatility of the coke may be reduced to less than 5 percent and the antiknock value of the distillate may be increased to an octane number of approximately 78. The motor fuel of improved antiknock value thus recovered may be equivalent to approximately 82 percent of the distillate subjected to retreatment.

It will be understood that the foregoing example illustrates only one of the many types of operation possible within the concepts of the present invention and should therefore not be construed as a limitation.

We claim as our invention:

1. A process for producing anti-knock motor fuel and coke which comprises subjecting a mixture of hydrocarbon oil and solid carbonaceous material to cracking conditions of temperature and pressure, separating the mixture into vapors and a mass of coke containing volatiles, fractionating the vapors to form a gasoline distillate, heating a portion of the gasoline to a temperature adequate to vaporize volatiles contained in the coke, and then passing the thus heated gasoline through said mass of coke.

2. In a process for the conversion of hydrocarbon oils and solid carbonaceous materials wherein a mixture of said materials is continuously subjected to conversion conditions in a heating coil and thence introduced into an enlarged reaction zone wherein coke containing volatiles deposits and from which vapors are withdrawn to subsequent fractionation to condense the products heavier than motor fuel distillate and the final vapors condensed and the motor fuel like distillate recovered, the improvement which comprises isolating said reaction zone from the system when a substantial body of said coke has deposited therein while continuing the discharge of said mixture from the heating coil into a second enlarged reaction zone, concurrently heating portions of the recovered motor fuel distillate sufficiently to vaporize volatiles contained in the coke and thence passing the same through the bed of coke in the isolated reaction zone for the purpose of substantially devolatilizing the coke and improving the antiknock character of the motor fuel distillate, removing the vaporous products from the devolatilizing zone,

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subjecting the same to condensation and collecting the resulting products.

3. The process as defined by claim 2 further characterized in that reflux condensate formed by said fractionation is passed through a second heating coil maintained at higher temperature than the first-mentioned heating coil and then

discharged into the first-mentioned reaction zone during the discharge of the heated mixture from the first-mentioned heating coil into this reaction zone.

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