April 30, 1935. C. W. ANDREWS ET AL 1,999,437

METHOD OF COKING HEAVY FLUENT HYDROCARBONS

Filed June 24, 1932 2 Sheets-Sheet 1

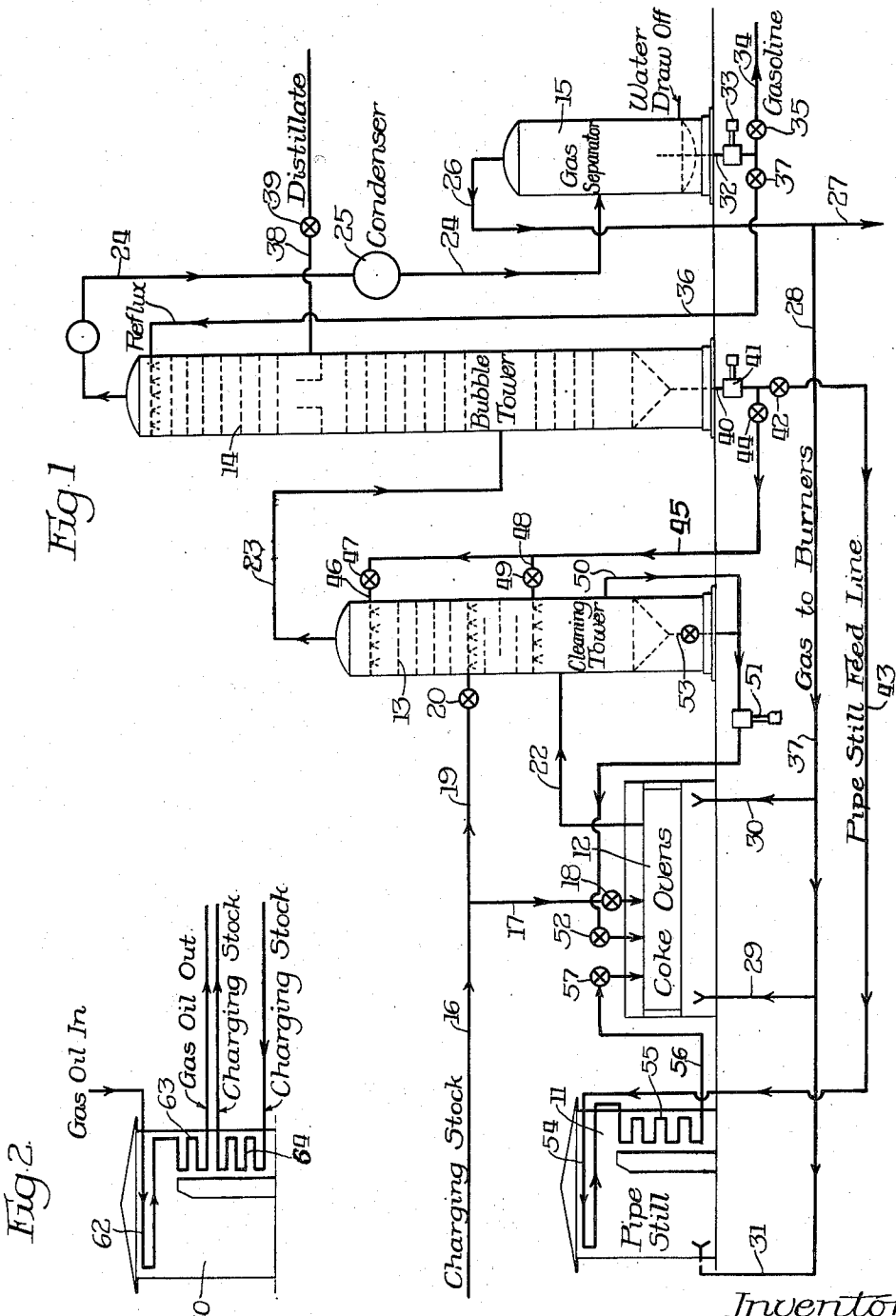


Fig. 1

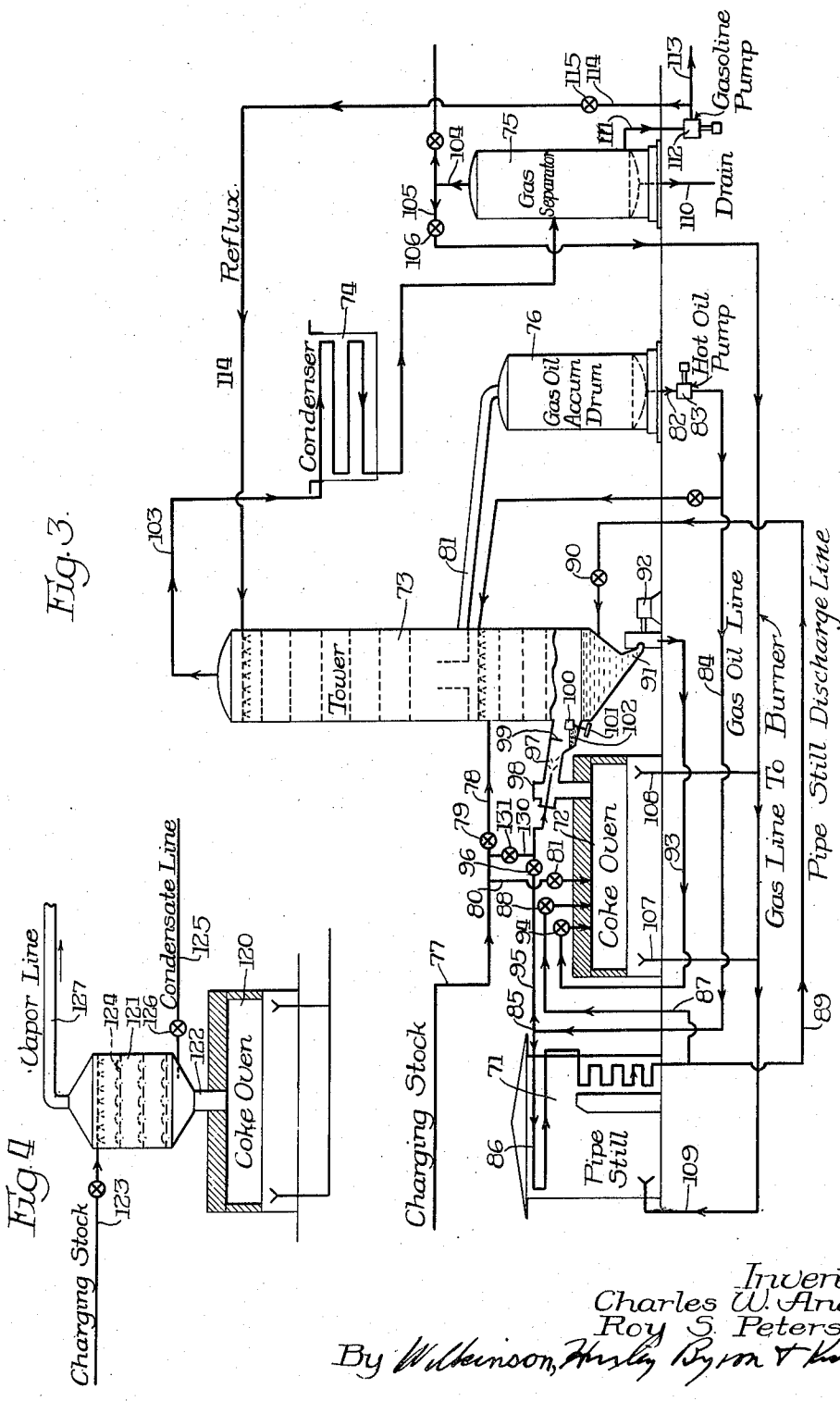
Fig. 2

Inventors:
Charles W Andrews
Roy S. Petersen
By Wilkinson, Huxley, Byron & Knight
Attys

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1,999,437

METHOD OF COKING HEAVY FLUENT HYDROCARBONS

Charles W. Andrews, Chicago, Ill., and Roy S. Petersen, San Antonio, Tex., assignors to Brassert-Tidewater Development Corporation, Chicago, Ill., a corporation of Delaware

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2 Claims. (Cl. 202—5)

This invention relates to a new and improved method of treating hydrocarbons. More specifically the invention relates to the coking of the non-volatile residues of petroleum hydrocarbons. The invention further involves the cracking of volatile portions of the hydrocarbons.

It is an object of the present invention to provide a new and improved method for the treatment of hydrocarbons and more particularly to the coking of petroleum hydrocarbons and the cracking of volatile constituents of the material being treated.

It is also an object to provide a method capable of being carried out at substantially atmospheric pressures.

It is an additional object to provide a method in which the solid residue may be recovered as a hard, dense coke of low volatile content.

It is a further object to provide a method whereby heat from intermediate stages of the process may be utilized for the purpose of topping the charging stock.

A further object is to separately preheat the charging stock and the recycle bottoms from the bubble tower whereby temperatures most suitable for the cracking of the two stocks may be maintained and thereafter discharging the streams into the coking ovens.

It is also an object of the invention, where under certain vapor phase conditions the carbon formed may not have sufficient liquid to form salable coke in the oven, to use the incoming charging stock either directly or through the cleaning tower to supply the necessary amount of liquid to properly bind the carbon particles into coke during the coking operation.

It is a further object to assist in coking charging stock by means of heat carried into the oven by the recycled condensate.

Other and further objects will appear as the description proceeds.

The assistance in coking charging stocks by means of the heat carried into the oven by the recycled condensate, is of great importance as many charging stocks will be found which cannot be satisfactorily preheated to a high enough temperature to permit of rapid coking and cracking in the oven. By our method we not only have the heat supplied through the floor of the oven, but also an additional supply of heat in the recycled condensate which has been heated to a temperature of at least 900° F. to 1000° F. and preferably higher, for heating, cracking and coking the incoming charging stock. It will be understood that if the recycled condensate is at liquid phase temperatures further cracking and coking will go on in the oven; if, however, it is heated to substantially vapor phase temperatures whereby gas, cracked vapors and carbon are formed, only a portion of the carbon will remain in the oven on account of the velocity of the gases carrying it forward into the cleaning tower. It is therefore a part of this invention to remove this carbon from the vapors as far as feasible and return it to the coking chamber. We do this by either using bottom condensate or charging stock as cleaning media, these streams being returned to the oven. Where charging stock is used as the cleaning medium it will be partially reduced in the operation. In forming coke under these conditions much, if not all of the carbon from the bottom condensate will become a part of the coke formed from the charging stock. The quality of the coke formed in the oven will, to a large extent be governed by the amount of heavy hydrocarbons in the return to the coke ovens from the cleaning tower.

We have shown somewhat diagrammatically certain preferred embodiments of apparatus adapted for carrying out our invention in the accompanying drawings, in which—

Figure 1 is a diagrammatic layout of apparatus, shown in elevation and partly in section, and flow sheet showing one preferred form;

Figure 2 is a fragmentary elevation showing a modification of the pipe still hookup of Figure 1;

Figure 3 is a view similar to Figure 1 and showing a modified form of construction; and

Figure 4 is a fragmentary elevation showing a modified form of apparatus adapted for use in connection with the coke oven charging and overhead offtake.

Referring first to the form shown in Figure 1, the apparatus includes the pipe still 11, coke ovens 12, cleaning tower 13, bubble tower 14 and gas separator 15. The charging stock line 16 is provided with the branch 17 controlled by valve 18, this branch leading to the coke oven. The line 16 is also provided with the branch 19 controlled by valve 20 leading to an intermediate portion of the cleaning tower 13. The vapor line 22 leads from the top of the oven 12 to a lower point in the cleaning tower 13. The line 23 leads from the top of the cleaning tower 13 to an intermediate portion of the bubble tower 14, this line carrying the vapors from the cleaning tower to the bubble tower.

The line 24 leads through condenser 25 to an intermediate portion of the gas separator 15.

T'e line 26 for carrying gas from the gas separator is provided with the branch 27 which may lead to any suitable gas holding or using apparatus (not shown). The line 26 is also provided with the branch 28 which, in turn, is provided with branches 29 and 30 leading to the heating flues of the coke oven, and with the branch 31 leading to the combustion chamber of the pipe still 11.

Gasoline from the gas separator 15 may be drawn off through line 32 by pump 33. This line 32 communicates with the gasoline draw-off line 34 controlled by valve 35. The line 32 also is connected to the gasoline reflux line 36 controlled by valve 37. This line 36 leads into an upper portion of the bubble tower 14.

A distillate take-off line 38 controlled by valve 39 leads off from an intermediate portion of the bubble tower 14. The bottom distillates from the bubble tower 14 are drawn off through line 40 by pump 41. This line 40 communicates through valve 42 with the pipe still feed line 43. It also communicates through valve 44 with the reflux line 45. This line 45 has a branch 46 controlled by valve 47 leading into the top of the cleaning tower 13. It also has a second branch 48 controlled by valve 49 leading into a lower portion of the cleaning tower 13. The line 50 leads from the lower portion of the cleaning tower 13, being adapted to draw off the heavy distillate. This line 50 includes the pump 51 and leads through valve 52 into the top of the coke oven 12. The bottom of the cleaning tower 13 is shown as provided with a lock 53 through which any heavy sludge or settlings in the bottom may be periodically removed, and the pump 51 is so placed as to handle the heavy sludge as well as the heavy distillate through line 50.

The pipe still feed line 43 connects to the radiant and convection sections 54 and 55 of the pipe still. The pipe 56 leads from the end of the pipe still coils to the coke oven, being controlled by valve 57. The cleaning tower 13 and bubble tower 14 have been shown as containing baffles or trays to assist in contact between the gases and liquids. The details of construction of these elements of the apparatus form no part of the present invention and any types of cleaning, refluxing and fractionating equipment may be used without departing from our invention.

In Figure 2 a modified form of connection to the pipe still 60 has been shown. The gas oil or condensate is handled through the gas oil line which connects to the radiant section 62 and a convection section 63. These sections may be connected in the form of construction shown in Figure 1 in a manner similar to sections 54 and 55 of pipe still 11. In addition a second convection section 64 is provided for use in heating the charging stock where that stock does not come from prior treatment apparatus at a temperature adequate for the present treatment. This convection section 64 could be connected in charging stock line 16 of the form shown in Figure 1.

The form of construction shown in Figure 3 includes the pipe still or heater 71, coke oven 72, cleaning tower 73, condenser 74, gas separator 75 and gas oil accumulating drum 76. The charging stock line 77 is provided with the branch 78 controlled by valve 79, this branch leading to the lower section of the cleaning tower 73. This line 77 is also provided with the branch 80 controlled by valve 81 leading into the top of the coke oven 72.

The tower 73 is provided with the gas oil or condensate draw-off passage 81 which leads into the top of the gas oil accumulating drum 76. This passage 81 is made of such size as to serve both as a draw-off for the condensate and to permit vapors from the drum 76 to return to the tower 73.

The draw-off line 82 at the bottom of drum 76 is provided with the pump 83 and with the line 84 which leads to the junction 85. The junction 85 is connected in one direction to the pipe still coil 86. The other end of this coil 86 is connected to the line 87 which leads into the top of the coke oven 72 through valve 88. The lower end of the pipe still coil 86 is also connected through line 89 and valve 90 to the bottom of the tower 73. The draw-off 91 at the bottom of tower 73 is provided with pump 92 adapted to force the material through line 93 and past valve 94 into the top of the coke oven 72.

The junction 85 on line 84 has a second connection to the line 95, which discharges through valve 96 into the passage 97 leading from standpipe 98. The standpipe 98 is connected to the upper portion of the coke oven 72. The passage 97 is provided with the division plate 99 which is adapted to aid in the control of the flow of the gases and vapors from the coke oven 72 to the bottom of the tower 73. The lower division member 100 co-acts with the adjustable valve 101 to maintain a sump of liquid 102 which co-acts with the plate 99 to define the passage area for the overhead products from the coke oven.

The line 103 carries the overhead products from tower 73 through condenser 74 to an intermediate portion of the gas separator 75. The gases leave the gas separator through pipe 104 and they pass through branch 105 controlled by valve 106 to the burners in the combustion passages in the coke oven through lines 107 and 108. The line 109 leads to the burner in the combustion space of the pipe still 71.

A water drain 110 is provided at the bottom of the gas separator 75. The gasoline line 111 leads from the side of the gas separator 75, this line being provided with the pump 112. The discharge side of the pump 112 leads through line 113 to any suitable gasoline holding or using apparatus (not shown). The line 114 controlled by valve 115 is adapted to carry reflux gasoline to the top of the cleaning tower 73.

Referring now to the form of construction shown in Figure 4, the coke oven 120 has a charging and cleaning chamber 121 connected to the top of the oven by passage 122. The charging stock line 123 enters the upper portion of the chamber 121. This chamber 121 is provided with the bubble trays or equivalent contact means 124. The line 125 controlled by valve 126 leads into the lower portion of the chamber 121, this line being adapted to introduce the highly heated condensate from further stages in the process.

The vapor line 127 leads from the top of the chamber 121 and is adapted to carry the overhead products to any desired fractionating or other apparatus (not shown) for further treatment of the products.

The form of construction shown in Figure 4 may be substituted in the form shown in Figure 3 or in the form shown in Figure 1. In either case, the contact chamber 121 may take the place of further apparatus. For example, in the construction of Figure 1, the contact chamber 121 may take the place of the cleaning tower 13. In the form of construction shown in Figure 3, the

contact chamber 121 may be substituted for the lower section of the cleaning tower 13.

In the operation of the apparatus as shown in Figure 1 to carry out our improved method of treatment charging stocks which usually are either gas oils, bottoms from oil topping operations or residues from oil cracking may be at sufficient temperatures as the result of previous operations to make preheating unnecessary. If not already at a sufficient temperature, preheating is desirable to a point usually in excess of 800° F. This preheating can be carried on either in a separate preheater or, as shown in Figure 2, in the convection section of a regular pipe still in which the radiant sections are being used to heat the recycle condensates from the bubble tower. The heating of the recycle stock may however be carried on in any suitable type of still separate from the charging stock heater. This step is an important element in our invention as it is well known that residues cannot be heated to as high a temperature as recycle condensates such as gas oils which are returned from the bubble tower. In a preferred method of operation we carry the temperature of the charging stock between 800° F. and 900° F. whereas the temperature of the recycled condensate would normally be at least approximately 900° F. and would preferably be from 1000° F. to 1100° F. or even higher if necessary to secure the desired amount of vapor phase cracking.

We prefer to use the charging stock in the cleaning tower for the first cleaning, although it may be discharged directly to the ovens through valve 18, if desired. The vapors passing off the coke ovens through line 22 carry with them entrained coke particles and tar globules or polymers which it is very desirable to remove before reaching the bubble tower. Where the charging stock does this satisfactorily, no further cleaning is necessary; otherwise gas oil from the bottom of the bubble tower passing through valve 47 will be used to further clean the vapors and remove as far as possible any objectionable matter.

The reflux to the top of the cleaning tower 13 through valve 47 also has the function of regulating the temperatures of the gases and vapors passing over to the fractionating or bubble tower 14. If the charging stock through line 19 and valve 20 functions, it will assist in cleaning the ascending vapors.

Different charging stocks will require different temperatures at the top of the cleaning tower and it is our purpose to maintain these at as high a temperature as is desirable, usually above 600° F., by maintaining the temperatures in the column. In some cases the charging stock will be at sufficient temperature to actually increase the temperature of the above vapors while in other cases it may be necessary to bring the vapors from the ovens at a higher temperature for the same purpose. We have provided inlets for gas oil through valve 49 should lower temperatures be required or it not be desirable to use charging stock in the cleaning tower.

The vapors pass over through line 23 to bubble tower 14. This tower may be of any conventional form and has for its purpose the production of suitable end point gasoline as an overhead and of gas oil suitable for further high temperature cracking or other disposition as a bottom condensate. We have shown a distillate side take-off 38 which has for its usual purpose the balancing of the operations so that no undue amount of distillate will build up in the condensate returning to the pipe still as the distillate usually requires a different temperature for cracking from that of the regular bottom condensates. Obviously distillate may be removed for other uses if so desired.

It is a feature of this invention to increase the temperatures in the coke ovens by preheating the condensate bottoms passing through line 43 in the pipe still 11 to as high temperatures as may be carried under good operating conditions. In some cases temperatures may be high enough to vaporize practically all the oil passing through the still rather than heating the oil in the liquid phase. Valve 57 would be used to control these operations as well as cutting off the oven from the supply.

Preferably the oven inlet through valve 57 connected with the pipe still is at the opposite end from the vapor outlet so that full advantage may be taken of the volume of the oven for the completion of the cracking reaction. The return from the cleaning tower through valve 52 and the direct charge through line 17 and valve 18 are also located at the same end as the connection through valve 57.

In operating the form of apparatus installation shown in Figure 3, part or all of the hot condensate is returned to the bottom of the cleaning tower. This tower may be a combination cleaning and bubble tower as shown in the drawings, this being accomplished by a dividing plate which enables the drawing off of the condensate of a desired specification, at the same time allowing the heavier tars and coke particles to fall to the bottom where they may be removed by the pump, and forced back into the oven for further treatment. In this case the charging stock is also used as a cleaning medium for the lower section of the tower, with an auxiliary supply of condensate from the gas oil accumulator drum should it be needed for better fractionation, or the condensate may be used in place of charging stock as a cleaning medium.

We have indicated a standpipe in which a spray of condensate or charging stock is used to cool the vapors coming from the ovens and at the same time check the objectionable deposits in the line. The line 130 controlled by valve 131 connects the charging stock line 78 with the line 95 leading into the standpipe 98. By use of this line the charging stock may be mixed with condensate through line 95 in going into the standpipe or the charging stock may also be used through the line 130 and discharge into the standpipe.

At the lower end of the standpipe is a diaphragm and an adjustable oil seal below it. The level of the oil seal may be raised or lowered by the valve 101 being opened or closed or maintained in an intermediate position automatically if desired. In this way suction on the oven may be regulated to whatever extent desired.

The hot return distillate preferably is injected tangentially below the level of the oil in the bottom of the cleaning tower 13 in order to keep the body of liquid in constant motion and thus prevent building up of carbon deposits. It will be understood that any free carbon present is sufficiently low in quantity so that the body remains liquid under the conditions of the method and that the liquid and any entrained carbon are discharged from the cleaning tower 13 in a liquid condition.

Figure 4 shows another method of accomplishing these results. In this case the cleaning tower is placed immediately on top of the oven, the

charging stock being used as a cleaning fluid. Trays or bubble caps may be used to obtain the desired results. The hot condensate is fed in below the lower tray and a large portion will immediately vaporize owing to its high temperature. These vapors passing upward along with the vapors produced in the oven will be cleaned by the incoming charging stock, and the charging stock will at the same time be heated materially by the hot vapors. The hot condensate which is not vaporized will flow down into the oven for further treatment together with the charging stock.

It will be noted that the forms of apparatus shown in Figures 1 and 3 are actually quite similar in operation and results obtained although they are somewhat different in appearance. In each there are separating and fractionating zones which are directly connected. In Figure 1 these zones are represented by cleaning tower 13 and bubble tower 14, while in Figure 3 they are represented by the portions below and above the draw off deck above which the passage 81 is connected. This passage 81 is, in general, the substantial equivalent of line 40 of Figure 1.

The ovens may be supplied in batteries of any desired number and charging of each oven in the battery continues until a desired depth of coke is formed in the oven. Feeding is then discontinued on this oven, the coke allowed to dry and then pushed out in the usual way, after which the oven is closed and the cycle starts again.

While we have shown a single pipe still, oven, cleaning tower and bubble tower, it will be understood that with a battery of ovens the other elements may be provided in any desired number. One still may serve a plurality of ovens and likewise each oven may have separate cleaning and fractionating apparatus or several ovens or the whole battery may be served by a single set of apparatus for handling the overhead products. The apparatus is shown diagrammatically in the drawings and it will be understood that it may be changed to meet varying conditions and requirements. We therefore contemplate such changes and modifications of both method and apparatus as come within the spirit and scope of the appended claims.

We claim:

1. The method of coking heavy fluent hydrocarbons which comprises introducing heavy liquid hydrocarbons into a fractionating means, admitting to the fractionating means an intermediate hydrocarbon condensate into contact with the heavy liquid hydrocarbons, the condensate being derived from the products of the fractionating means, heating said condensate before return to the fractionating means to a materially higher temperature, such as 900° F., than that of the heavy hydrocarbons, whereby heat from the condensate supplies heat to the mixed bottoms in the fractionating means and separates sufficient lighter fractions from the heavy hydrocarbons to form a charging stock largely free from lighter fractions at a temperature above 600° F. and at a concentration of coking constituents sufficiently low to effect the discharge of bottoms in a liquid condition, discharging the bottoms into a coking chamber, and heating externally the coking chamber to add substantially all the further heat necessary for coking, and producing a hard, dense coke.

2. The method of coking heavy fluent hydrocarbons which comprises introducing heavy liquid hydrocarbons into a separating and fractionating zone, admitting to the separating and fractionating zone an intermediate hydrocarbon condensate into contact with the heavy liquid hydrocarbons, the condensate being derived from the products of the fractionating zone, heating said condensate before return to the separating and fractionating zone to a materially higher temperature, such as 900° F., than that of the heavy hydrocarbons, whereby heat from the condensate supplies heat to the mixed bottoms in the separating and fractionating zone and separates sufficient lighter fractions from the heavy hydrocarbons to form a charging stock largely free from lighter fractions at a temperature above 600° F. and at a concentration of coking constituents sufficiently low to effect the discharge of bottoms in a liquid condition, discharging the bottoms into a coking member, heating externally the coking chamber to add substantially all the further heat necessary for coking, and producing a hard, dense coke, and returning condensate from the overhead from the coking chamber to the initial separating and fractionating zone.

CHARLES W. ANDREWS.
ROY S. PETERSEN.

CERTIFICATE OF CORRECTION.

Patent No. 1,999,437. April 30, 1935.

CHARLES W. ANDREWS, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 4, second column, line 42, claim 2, for "member" read chamber; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 25th day of June, A. D. 1935.

Bryan M. Battey

(Seal) Acting Commissioner of Patents.