June 29, 1954 H. A. DUTCHER 2,682,497

PEBBLE HEATER AND METHOD OF CONVERTING HYDROCARBONS

Filed April 10, 1950 2 Sheets-Sheet 1

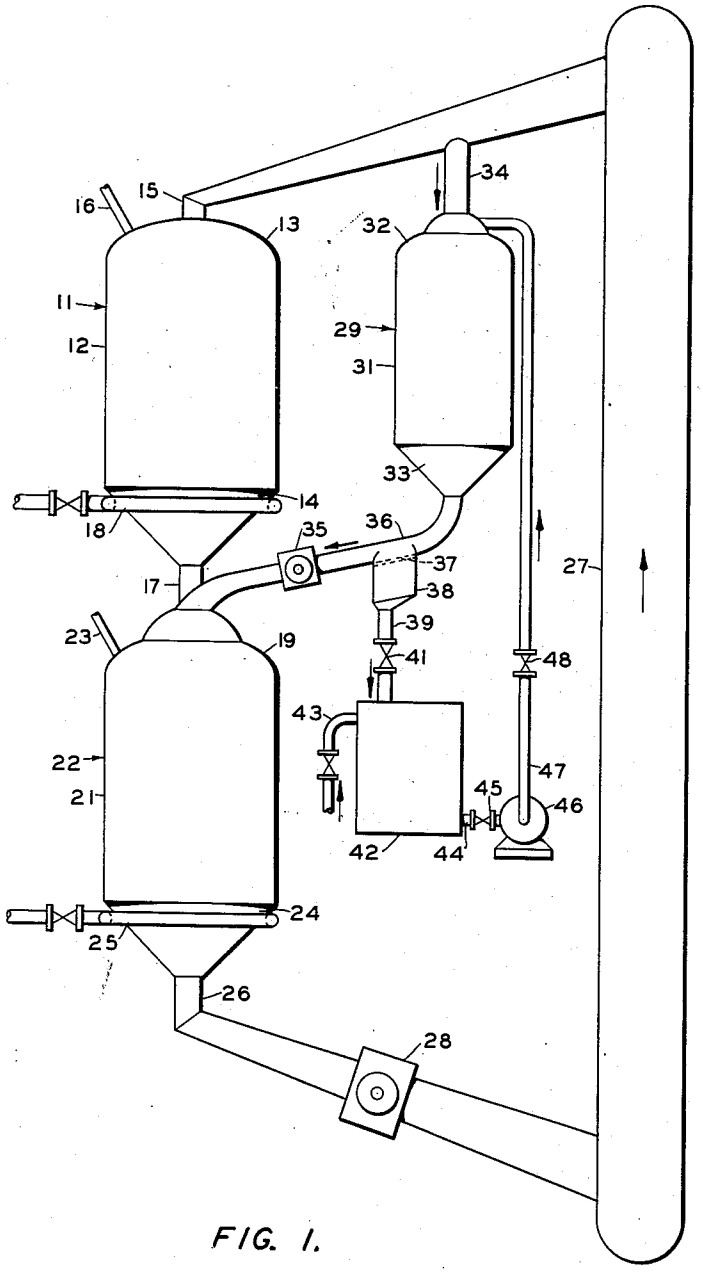


FIG. 1.

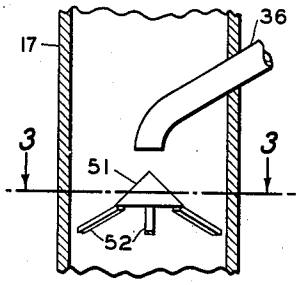


FIG. 2.

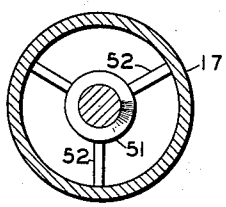


FIG. 3.

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PEBBLE HEATER AND METHOD OF CONVERTING HYDROCARBONS

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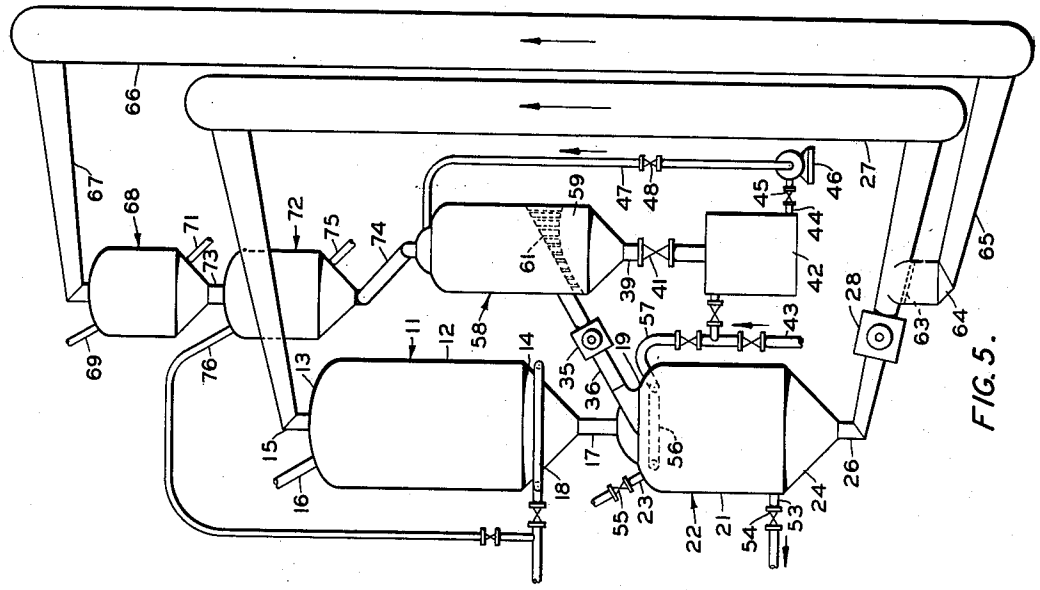


FIG. 5.

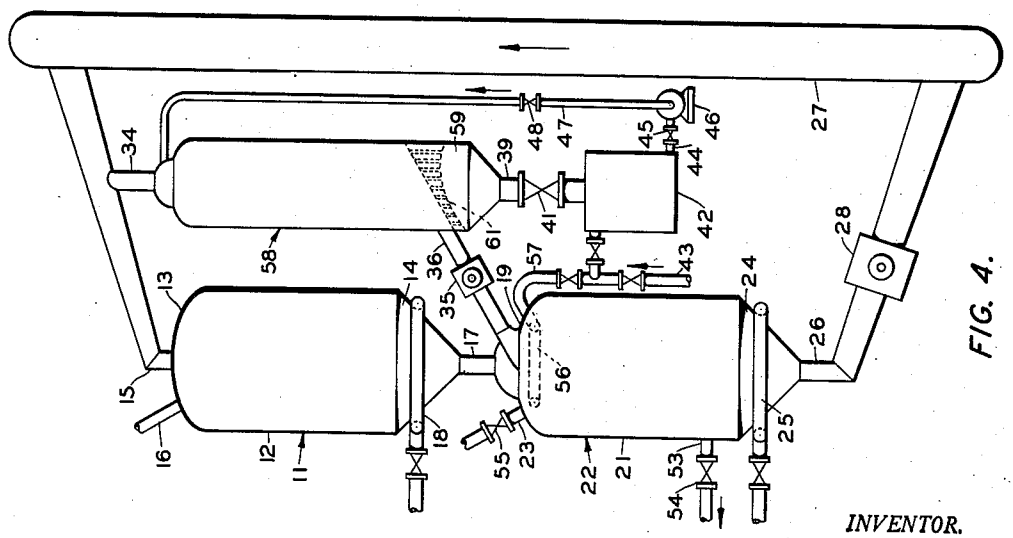


FIG. 4.

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PEBBLE HEATER AND METHOD OF CONVERTING HYDROCARBONS

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Application April 10, 1950, Serial No. 155,037

13 Claims. (Cl. 196—55)

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This invention relates to pebble heat exchangers. In one of its more specific aspects, it relates to the conversion of heavy petroleum oil or residuum. In another of its more specific aspects, it relates to a means for introducing heavy petroleum oil into a reaction chamber. In another of its more specific aspects, it relates to improved pebble heat exchange apparatus.

Thermal conversion processes which are carried out in so-called pebble heater apparatus utilize a fluent mass of solid heat exchange material, which mass is ordinarily heated to a high temperature by passing hot gas therethrough in a first direct heat exchange step and is then caused to contact fluid reactant materials, furnishing heat thereto in a second direct heat exchange. In the conversion of heavy petroleum oils in pebble heater apparatus, it is known to introduce a stream of the heavy petroleum oil or residuum as reactant material directly into the upper portion of a reaction chamber which contains a fluent mass of pebbles heated as above described. In such operation, it has been found that a very poor distribution of the heavy petroleum fraction is obtained throughout the reaction chamber and the hot fluent pebble mass contained therein. Another problem which has been encountered in such an operation is that excessive coking occurs by reason of the direct contact between the heavy petroleum fraction and the heated pebbles. For the above reasons non-uniform conversion of the heavy petroleum oil is obtained and an excessive amount of such oil is converted to coke rather than to the desired lighter hydrocarbon materials.

Broadly speaking, this invention comprises a means and method for converting heavy petroleum oils to lower boiling hydrocarbon materials, such as ethylene, propylene, and highly aromatic gasoline-type materials. The means by which this improved operation is obtained is an improved pebble heater apparatus which utilizes the conventional 2-chamber device but which has, in addition, at least one other pebble chamber which is utilized for coating pebbles which are at a relatively low temperature with the heavy petroleum oil utilized as the heavy reactant material charge stock for the system. The method of converting the heavy petroleum oil fraction to the lower boiling hydrocarbon materials has the improvement of better distribution of the oil throughout the reaction chamber and a lesser direct contact between the oil charge stock and the hot pebbles from the pebble heater chamber.

Conventional pebble heater chambers of pebble heater apparatus are generally formed as cylinders in which a solid heat exchange material is collected in the form of a moving bed. Hot heat exchange gases are passed upwardly through the cylindrical bed, sometimes being introduced thereinto at the periphery of the bed and at its lower end, and sometimes through a refractory arch which supports the moving pebble bed. At other times, heat is supplied to the heating chamber by supplying a fuel to the lower portion of the pebble bed within the heater chamber and burning the fuel on the surface of the pebbles so as to heat the pebbles by combustion and further heat the pebbles by passing the resulting combustion gas upwardly through the downflowing fluent mass of pebbles and in direct heat exchange therewith.

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The heated pebbles are introduced into the upper portion of a reaction chamber and the reactant materials when comprising heavy petroleum oil or residuum have been conventionally introduced as a fluid stream directly onto the surface of the hot pebbles from the pebble heater chamber and flow downwardly through the reaction chamber concurrent the flow of the hot solid heat exchange material, thereby obtaining the heat necessary for thermal conversion of the heavy petroleum or residuum fraction.

Solid heat exchange material which is conventionally used in pebble heater apparatus is generally called "pebbles." The term "pebbles" as used herein denotes any solid refractory material of flowable size and form, having strength which is suitable to carry large amounts of heat from the pebble heating chamber to the reaction chamber without rapid deterioration or substantial breaking. Pebbles which are satisfactorily used in pebble heater apparatus are ordinarily substantially spherical in shape and range from about ⅛ inch to about 1 inch in diameter. In high temperature processes, pebbles having a diameter of between about ⅛ inch and ½ inch are preferred. The pebbles must be formed of a refractory material which will withstand temperatures at least as high as the highest temperature attained in the pebble heater chamber. The pebbles must also be capable of withstanding temperature changes within the apparatus. Refractory materials, such as metal alloys, ceramics, or other satisfactory material may be utilized to form such pebbles. Silicon carbide, alumina, periclase, thoria, beryllia, Stellite, zirconia, and mullite may be satisfactorily used to form such heat transfer pebbles or may be used in admixture with each other or with other ma-

terials. Pebbles formed of such materials when properly fired serve very well in high temperatures. Some pebbles, such as mullite-alumina pebbles withstand temperatures as high as 3200° F. and above.

An object of this invention is to provide an improved pebble heater apparatus. Another object of the invention is to provide improved means for introducing a heavy petroleum fraction charge stock into a reaction chamber of pebble heater apparatus. Another object of the invention is to provide a method for introducing a heavy petroleum fraction charge stock into a reaction chamber of pebble heater apparatus. Another object of the invention is to provide improved means for reducing coke formation in the thermal conversion of a heavy petroleum fraction charge stock. Another object of the invention is to provide an improved method for reducing coke formation in the thermal conversion of a heavy petroleum oil charge stock. Other and further objects and advantages will be apparent to those skilled in the art upon study of the accompanying discussion and the drawings.

Understanding of the invention will be facilitated upon reference to the drawings in which Figure 1 is a diagrammatic elevation of the pebble heater apparatus of this invention. Figure 2 is a modification of the pebble throat arrangement between the pebble heater chamber and reaction chamber of the device shown as Figure 1 of the drawings. Figure 3 is a horizontal cross-section taken along the line 3—3 of Figure 2. Figure 4 is a schematic showing of a preferred modification of the pebble heater apparatus of this invention. Figure 5 is another diagrammatic elevation of a modification of the pebble heater device of this invention.

Referring specifically to Figure 1 of the drawings, pebble heater chamber 11 comprises outer shell 12, which is closed at its upper and lower ends by closure members 13 and 14, respectively. Pebble inlet conduit 15 and gaseous effluent outlet conduit 16 are provided in closure member 13 and pebble outlet conduit 17 extends downwardly from closure member 14. Heating fluid inlet conduit 18 extends from a heating material supply source to closure member 14 and is preferably formed as a bustle ring extending around at least a portion of closure member 14, communicating through that closure member with the interior of pebble heater chamber 11. Pebble outlet conduit 17 in the lower end portion of chamber 11 has an enlarged cross-section in its lower end portion, which enlarged conduit portion is connected to closure member 19 in the upper end of shell 21 which forms reaction chamber 22. Gaseous effluent outlet conduit 23 is provided in closure member 19. The lower end portion of shell 21 is closed by closure member 24 and fluid conduit 25 is connected to closure member 24, communicating through that closure member with the interior of pebble chamber 22. Conduit 25 preferably extends as a bustle ring at least a portion of the way around closure member 24. Pebble outlet conduit 26 is provided in closure member 24, which pebble outlet conduit is connected at its lower end with the lower end portion of elevator 27. Pebble flow controller 28, which may be a conventional star valve, a table feeder, a gate valve, or the like, is provided intermediate the ends of pebble outlet conduit 26. Elevator 27 is connected at its upper end portion with pebble inlet conduit 15 which is connected at its lower end with closure member 13 of pebble heater chamber 11. Elevator 27 may be of a bucket type, a helical conveyor, a gas-life type elevator, or the like.

Contact chamber 29, which comprises shell 31 closed at its upper and lower ends by closure members 32 and 33, respectively, is connected to conduit 15 intermediate its ends by conduit member 34 which is connected to chamber 29 at closure member 32. Pebble outlet conduit 36 extends between closure member 33 of shell 31 and the enlarged portion of conduit 17 between the bottom of chamber 11 and the upper end portion of chamber 22. Pebble flow controller 35 is provided intermediate the ends of pebble conduit 36. A perforate member 37 is provided in the lower portion of a section of outlet conduit 36 and collector chamber 38 is affixed to the lower portion of conduit 36 and around perforate member 37 therein. Fluid outlet conduit 39, which is provided with flow control valve 41, extends between the lower end portion of collector chamber 38 and charge stock storage chamber 42. Charge stock supply conduit 43 extends into storage chamber 42 and charge stock outlet conduit 44, which is provided therein with flow control valve 45, extends between the lower portion of storage chamber 42 and pump 46. Charge stock supply conduit 47 extends between pump 46 and the lower end portion of pebble conduit 34 which is connected at its lower end with contact chamber 29. Flow control valve 48 is provided intermediate the ends of charge stock supply conduit 47.

In the operation of the device disclosed above, pebbles are supplied to the upper end portion of pebble heater chamber 11 and form a fluent contiguous mass with that chamber, which fluent pebble mass gravitates downwardly through that chamber. A fluid heating material is introduced into the lower portion of chamber 11. The fluid heating material may be a hot combustion gas which is introduced into the lower portion of chamber 11 through inlet conduit 18. The combustion gas flows upwardly through that chamber countercurrent the flow of solid heat exchange material therein. The heating material may also by a combustible fuel, together with air, which fuel is burned in the presence of the fluent pebbles, imparting heat to those pebbles as a result of the combustion. Resulting combustion gases are allowed to flow upwardly through chamber 11 countercurrent the flow of pebbles therein. The hot combustion gas heats the pebbles in a direct heat exchange relation and after imparting a large portion of its heat to such pebbles, the gaseous effluent material is removed from chamber 11 through effluent outlet conduit 16. The pebbles are heated to a temperature within the range of 2000° F. to 3200° F., preferably within the range of 2500° F. to 3000° F., in chamber 11 and are gravitated from that chamber through conduit 17 into reaction chamber 22 in which they form a fluent contiguous pebble bed.

A second portion of pebbles is introduced into chamber 29 through conduit 34 and forms a fluent contiguous mass within that chamber. Heavy petroleum oil or residuum is pumped by means of pump 46 through conduit 47 and is sprayed onto the surface of the pebbles which are introduced into chamber 29. The heavy petroleum oil generally has an API gravity within the range of 10 to 25, preferably between 15 and 20. The pebbles within chamber 29 are at a temperature within the range of from 300° F. to 800° F. It is preferred that the temperature of those pebbles

be maintained within the range of from 350° F. to 700° F. As the pebbles are introduced into chamber 29, the heavy petroleum fraction is sprayed onto the surface of those pebbles and as the mass of pebbles moves downwardly through chamber 29 the coating of oil is evenly distributed over the surface of the individual pebbles. The oil coated pebbles are gravitated from the lower portion of chamber 29 through conduit 36. As the oil coated pebbles flow through conduit 36, any excess heavy oil or residuum which is not intimately coating the pebbles is separated from the pebbles and passes into an excess oil separation means comprising perforate member 37 and collector chamber 38. The oil is removed from chamber 38 through conduit 39 into storage chamber 42. The oil is then recycled to the upper portion of chamber 29 through conduit 44, pump 46, and conduit 47.

The oil coated pebbles are introduced into the enlarged portion of conduit 17 and flow downwardly in admixture with the heated pebbles from pebble heater chamber 11. The heated pebbles and the oil coated pebbles are evenly distributed as they gravitate together into reaction chamber 22. The heated pebbles from pebble heater chamber 11 provide the heat necessary for the conversion of the coating of heavy oil on the pebbles from chamber 29. The heavy oil is raised to reaction temperature at a slightly slower rate than is obtained in the introduction of such oil directly onto the hot surface of the highly heated pebbles. For that reason, a considerably greater portion of the heavy residuum or petroleum oil is converted to hydrocarbon materials of lower boiling point than the residuum than was possible in the conventional method of direct introduction of heavy petroleum onto the highly heated pebbles. A smaller proportion of coke is formed in this manner than by the method of direct introduction of residuum onto highly heated pebbles. Resulting reaction products which are in a gaseous or vaporous state are removed from chamber 22.

Removal of the reaction products may be made through gaseous effluent outlet conduit 23 in closure member 19 or may be through fluid conduit 25. In the preferred method of operation, the gaseous effluent is removed through conduit 23 and a gaseous material, generally one which is inert to the reaction being carried on within chamber 22, is introduced into the lower portion of that chamber through conduit 25. Steam or a normally gaseous hydrocarbon, such as propane or butane, is satisfactorily utilized as the inert material introduced through conduit 25. The introduction of such gaseous material into the lower portion of the pebble bed within chamber 22 materially reduces the temperature of the pebble mass by extracting heat therefrom, which heat is carried into the upper portion of the pebble bed within chamber 22 by the inert gaseous material and the inert gaseous material is subsequently removed from chamber 22 through gaseous effluent outlet conduit 23. The pebbles which have been cooled by the reaction and heat exchange within chamber 22 are removed from that chamber through conduit 26 and the flow thereof is controlled through conduit 26 by means of pebble flow control device 28 which may be, as pointed out above, a conventional star valve, a table feeder, a gate valve, or other conventional flow control device. The pebbles, which have been cooled for better handling, are elevated by elevator 27 and are introduced into the upper end portion of conduit 15. A portion of these cool pebbles is removed from conduit 15 through conduit 34. The flow of pebbles through chamber 29 is controlled by means of pebble flow controller 35 in conduit 36. The remaining portion of the pebbles is introduced into the upper portion of chamber 11 through conduit 15 and the pebbles are raised to a high temperature therein as described above.

Referring particularly to Figure 2 of the drawings, conduit 17 is modified by providing it with a baffle member 51 which is supported therein by support members 52. Baffle member 51 is smaller in diameter than the inner diameter of conduit 17 by more than at least two pebble diameters. Conduit 36 extends through the wall of conduit 17 and terminates at a point directly above baffle member 51. The disposition of baffle member 51 with respect to conduit 17 is shown in Figure 3 of the drawings. Baffle member 51 is preferably disposed so as to form an annulus between its periphery and conduit 17. Excellent admixing between hot pebbles which pass downwardly through conduit 17 and oil coated pebbles which gravitate into conduit 17 through conduit 36 is aided by baffle member 51.

Referring particularly to the device set forth as Figure 4 of the drawings, parts which are the same as those disclosed in connection with Figure 1 of the drawings, are indicated by like numerals. Chamber 22 of Figure 4 is provided intermediate its ends with effluent outlet conduit 53 which has flow control valve 54 provided therein. Conduit 53 is preferably provided in the lower portion of chamber 22 so that it can be adapted for the withdrawal of gaseous effluent from that chamber under conditions such that concurrent flow of solid heat exchange material and reaction products is obtained. Flow control valve 55 is provided in effluent outlet conduit 23 in closure member 19 of chamber 22. By such construction, it is possible to remove the gaseous reaction products from either the upper end portion of reaction chamber 22 or from a point in the lower portion of that chamber. Auxiliary reactant material inlet conduit 56 is shown by dotted lines in the upper end portion of reaction chamber 22 and surrounds a space adjacent the outlet end of conduit 17. Inlet conduit 56, which is preferably in the form of a perforate header, is connected to reactant material supply conduit 43 36 is aided by baffle member 51.

Contact chamber 58 differs from contact chamber 29 of Figure 1 in the incorporation of the collector chamber portion 59 at the lower end of chamber 58, which collector chamber portion corresponds to chamber 38 shown in Figure 1 of the drawings. Collector chamber portion 59 is separated from the upper portion of chamber 58 by means of a perforate pebble support member 61 which slopes downwardly across chamber 58 to the inlet end of pebble outlet conduit 36.

Operation of the device shown as Figure 4 of the drawings is similar to that set forth in the discussion of Figure 1 and differs particularly in the introduction of additional reactant material directly onto the surface of the pebbles which are introduced into the upper portion of chamber 22. Although it is realized that such operation results in a considerably higher carbon formation, it is at times desirable to feed a greater quantity of reactant material to the reaction chamber than is carried on the surface of the pebbles from contact chamber 58. Variation of the amount of reactant material fed to reaction chamber 22 on the

surface of the relatively cool pebbles from chamber 58 is obtained by varying the speed at which pebble flow controller 35 is operated. The ratio of oil coated pebbles from chamber 58, or chamber 29 of Figure 1, to the heated pebbles from chamber 11 is preferably maintained within a ratio of between 1:1 to 1:3. The ratio of hot to oil coated pebbles and the quantity of oil introduced through inlet conduit 56 is such that the heavy oil is raised to a reaction temperature within the range of from 1400° F. to 1600° F.

Although greater carbon formation is encountered by introducing the reactant material directly onto the surface of the pebbles in the upper portion of chamber 22 than is encountered when all of the oil is distributed as a coating on cool pebbles, a lesser amount of carbon formation is encountered than in an operation in which all of the heavy petroleum fraction is introduced directly onto the surface of pebbles which have been heated to a high temperature. This mixed type of operation, however, lends flexibility to the over-all process of this invention.

Gaseous material which may be inert to the reaction carried on within chamber 22 is introduced into the lower portion of that chamber through conduit 25 and when the gaseous reactant materials are withdrawn from chamber 22 through conduit 53 the inert gaseous material is also withdrawn through that conduit. When reaction products are withdrawn through effluent outlet conduit 23 the inert gaseous material is withdrawn either through conduit 23 or through conduit 53. The cooled pebbles from chamber 22 are elevated by elevator 27 in the same manner as described in the discussion of the device of Figure 1 of the drawings and the pebbles are supplied through conduit 34 and through conduit 15 in the same manner as described in connection with the device set forth as Figure 1 of the drawings. Heavy petroleum oil which is not retained on the surface of pebbles within contact chamber 58 is separated from those pebbles and is allowed to pass into an excess oil separation means which comprises perforate pebble support member 61 and collector chamber 59. The oil is passed therefrom through conduit 39 into storage chamber 42.

Referring particularly to the device set forth in Figure 5 of the drawings, parts which are the same as those described in connection with Figures 1 and 4 of the drawings are indicated by like numerals. This device differs from those described above in that a perforate member 63 is provided in a section of pebble outlet conduit 26, preferably downstream of pebble flow controller 28. The perforations in that conduit section are of such size as to allow pebbles of a particular size to fall therethrough. It is preferred that pebbles having diameters in the range between ⅛ inch and ¼ inch be allowed to fall therethrough, while pebbles having diameters of ⅜ inch and larger will be retained within conduit 26 by perforate conduit member 63. Perforations in conduit member 63 generally range between $\frac{3}{16}$ inch and $\frac{5}{16}$ inch. Pebble collector chamber 64 is provided around the perforate conduit member 63 so as to collect the smaller diameter pebbles which pass through the perforate conduit member, and pebble conduit 65 extends between pebble collector chamber 64 and the lower end portion of elevator 66 which is similar to elevator 27. Elevator 66 is attached at its upper end portion to pebble conduit 67 which is in turn connected at its lower end portion to regeneration chamber 68. Gaseous effluent conduit 69 is provided at the upper end portion of chamber 68 and air inlet conduit 71 is provided in the lower end portion of that chamber. Gas heating chamber 72 is provided below chamber 68 and is connected thereto by pebble conduit 73. Pebble outlet conduit 74 extends from the lower end portion of gas heating chamber 72 to the upper end portion of contact chamber 58. Air inlet conduit 75 is connected to the lower end portion of gas heating chamber 72. Air outlet conduit 76 extends from the upper end portion of chamber 72 to heating material inlet conduit 18 at the lower end portion of pebble heater chamber 11. Reactant material inlet conduit 47 is connected at its outlet end to the lower end portion of pebble outlet conduit 74 at a point adjacent its inlet to contact chamber 58.

In the operation of the device set forth as Figure 5 of the drawings, pebbles having a diameter of between ⅜ inch and 1 inch are introduced into the upper portion of chamber 11 and are heated in that chamber as described above. Pebbles having a diameter of between ⅛ inch and ¼ inch are introduced into the upper portion of contact chamber 58 and are coated with the heavy petroleum charge stock as described above. Excess oil is separated from the oil coated pebbles in chamber 58 as described in connection with the device of Figure 4 of the drawings, and the oil coated pebbles are introduced into chamber 22, together with the highly heated pebbles from chamber 11 and are admixed therein for reaction purposes as heretofore described. Resulting reaction materials may be withdrawn through effluent outlet conduit 23 or effluent outlet conduit 53.

No heat control gas is introduced into chamber 22 for the purpose of lowering and maintaining the temperature of pebbles therein. The pebbles are withdrawn from the lower end portion of chamber 22 through conduit 26 and the flow thereof is controlled by pebble flow controller 28. The pebbles of smaller diameter are separated from pebbles of a larger diameter as they flow over the perforate conduit section 63, the smaller pebbles being gravitated therethrough into pebble collector chamber 64. The larger pebbles are elevated by means of elevator 27 and are introduced into the upper portion of chamber 11. The smaller pebbles are supplied by conduit 65 to the lower portion of elevator 66 by which they are elevated to the upper end portion of conduit 67 through which they are gravitated into the upper portion of regeneration chamber 68. Air is introduced into the lower portion of regeneration chamber 68 through conduit 71 and any carbonaceous or tarry material is oxidized from the surface of the pebbles and gaseous effluent material is removed from regeneration chamber 68 through effluent conduit 69.

The pebbles from which the carbonaceous or tarry material has been removed are gravitated through conduit 73 into chamber 72. Air is introduced into the lower portion of chamber 72 through inlet conduit 75 and flows upwardly therethrough countercurrent the flow of pebbles therein. The pebbles are cooled in a direct heat exchange with the air in chamber 72 and are supplied in that cooled condition to the upper portion of chamber 58 through conduit 74. The air which is heated in the direct heat exchange in chamber 72 is supplied by conduit 76 to

heating material inlet conduit 18 wherein it is admixed with a combustible fuel material.

It is obvious that the air and fuel could be supplied to a combustion zone external of pebble heater chamber 11, but for the purpose of simplicity Figure 5 diagrammatically shows a common conduit for fuel and air into the lower portion of chamber 11. Reactant material is introduced onto the surface of the cooled pebbles at the lower end portion of conduit 74. A heating means, either externally or internally positioned may be provided in heat exchange relation with the lower portion of charge stock storage chamber 42. In most situations, that will not be necessary, however, for the oil separated from pebbles within chambers 29 and 58 will ordinarily carry sufficient heat to maintain the temperature of the oil in chamber 42 in a flowable state.

Specific example

A heavy residual oil having an API gravity of 17.9 is sprayed into the upper portion of a contact chamber and onto the surface of pebbles which are at a temperature of about 700° F. The oil is introduced into the contact chamber at a rate of about 50 pounds per hour. The oil coated pebbles are gravitated through the contact chamber and into the upper portion of a reaction chamber at a rate of about 600 pounds per hour, carrying about 42.5 pounds of oil per hour. Steam is introduced into the lower portion of the reaction chamber at a rate of about 43 pounds per hour and pebbles which are at a temperature of about 2500° F. are gravitated into the upper portion of the reaction chamber in admixture with the oil coated pebbles at a rate of about 1400 pounds per hour. Heat from the hotter pebbles raises the oil within the reaction chamber to a reaction temperature such that vaporous and gaseous products, amounting to about 93.4 weight per cent of the feed, are obtained by withdrawing them together with the steam from the upper portion of the reaction chamber. The type of products produced and their relative amounts are set forth as follows (weight per cent based on the feed):

	Percent
Gases (C_4 and lighter hydrocarbons, and H_2)	22.4
Gasoline (400° F. end point)	18.5
Light gas oil (400° F.–750° F.)	10.7
Heavy gas oil (750° F.–900° F.)	10.9
Higher boiling materials (900° F.+)	30.9

The composition of the gaseous products (C_4 and lighter) is shown in the following tabulation:

	Mol percent
H_2	10.6
CH_4	27.5
C_2H_4	26.5
C_2H_6	9.6
C_3H_6	15.3
C_3H_8	1.5
C_4's	8.4
C_4H_{10}	0.4

A portion of the feed material is converted to coke (about 6.6 weight per cent of the feed under these conditions) and is deposited on the surface of the pebbles. A portion of the coke bearing pebbles which have been reduced to a temperature of about 700° F. within the reaction chamber are returned to the contact chamber in which they are once again coated with heavy oil. The remaining portion of coke bearing pebbles are passed to a pebble heating chamber in which the coke is burned from the surface thereof, the coke supplying a portion of the fuel required of the process. In this manner, an excessive accumulation of coke on the pebbles is prevented. The presence of coke on some of the pebbles passing through the reaction chamber does not interfere with the formation of the oil coating on such pebbles and random distribution of the coked pebbles between the contact and heating chambers of the system insures adequate coke removal from the system.

Various modifications of this invention will be apparent to those skilled in the art upon study of the above disclosure and the drawings. Such modifications will be apparent to those skilled in the art and are believed to fall within the spirit and scope of this disclosure.

I claim:

1. A method for converting a heavy petroleum fraction to lighter hydrocarbon materials which comprises in combination the steps of passing a first portion of pebbles into the upper portion of a pebble heating zone; passing a hot fluid heating material through said heating zone so as to raise said first pebbles to a temperature within the range of from 2000° F. to 3200° F.; removing gaseous effluent materials from said pebble heating zone; passing said heated first pebbles into a reaction zone; by-passing said heating zone with a second portion of pebbles and introducing said second portion of pebbles into a contact zone; introducing said heavy petroleum into said contact zone and coating said second pebbles with only said heavy petroleum; passing said petroleum coated second pebbles from said contact zone into said reaction zone at a temperature within the range of from 300° F. to 800° F.; admixing said heated first pebbles and said petroleum coated second pebbles in said reaction zone and raising said heavy petroleum to reaction temperature thereby; removing gaseous reaction products from said reaction zone; removing said pebbles from said reaction zone; returning a first portion of said pebbles to said pebble heating zone; and returning the balance of said pebbles to said contact zone.

2. A method for converting a heavy petroleum fraction to lighter hydrocarbon materials which comprises in combination the steps of passing a first portion of pebbles into the upper portion of a pebble heating zone; passing a hot gaseous heating material through said heating zone so as to raise said first pebbles to a temperature within the range of from 2500° F. to 3000° F.; removing gaseous effluent material from said pebble heating zone; passing said heated first pebbles into the upper portion of a reaction zone and downwardly therethrough; by-passing said heating zone with a second portion of pebbles and introducing said second portion of pebbles into a contact zone; introducing said heavy petroleum into said contact zone and coating said second pebbles with only said heavy petroleum; passing said petroleum coated second pebbles from said contact zone into said reaction zone at a temperature within the range of from 350° F. to 700° F.; admixing said heated first pebbles and said petroleum coated second pebbles in said reaction zone and thereby raising said heavy petroleum to reaction temperature within the range of from 1250° F. to 1600° F.; removing gaseous reaction products from said reaction zone; removing said pebbles from the lower por-

tion of said reaction zone; returning a first portion of said pebbles to the upper portion of said pebble heating zone; and returning the balance of said pebbles to said contact zone.

3. The method of claim 2, wherein the ratio of said petroleum coated second pebbles to said heated first pebbles is within the range of from 1:1 to 1:3.

4. The method of claim 2, wherein the temperature of said second petroleum coated pebbles and said heated first pebbles at the point of introduction into said reaction zone and the ratio between said second and first pebbles is such that said heavy petroleum is raised to a reaction temperature within the range of 1400° F. to 1600° F.

5. The method of claim 2, wherein heavy petroleum in addition to that coating said second pebbles is introduced into the upper portion of said reaction zone; and the temperature of said second petroleum coated pebbles and said heated first pebbles at the point of introduction into said reaction zone, the ratio between said second and first pebbles, and the quantity of said additional heavy petroleum is such that said heavy petroleum is raised to a reaction temperature within the range of 1400° F. to 1600° F.

6. A method for converting a heavy petroleum fraction, having an API gravity within the range of 10 to 25, to lighter hydrocarbon materials which comprises in combination the steps of passing a first portion of pebbles into the upper portion of a pebble heating zone; passing a hot gaseous heating material through said heating zone so as to raise said first pebbles to a temperature within the range of from 2500° F. to 3000° F.; removing gaseous effluent material from said pebble heating zone; passing said heated first pebbles into the upper portion of a reaction zone and downwardly therethrough; by-passing said heating zone with a second portion of pebbles and introducing said second portion of pebbles into the upper portion of a contact zone and downwardly therethrough; introducing said heavy petroleum into the upper portion of said contact zone; passing said heavy petroleum downwardly through said contact zone in direct contact with said second pebbles, thereby coating said second pebbles with only said heavy petroleum; separating said petroleum coated second pebbles and excess petroleum; returning said excess petroleum to the upper portion of said contact zone; passing said petroleum coated second pebbles from said contact zone into said reaction zone at a temperature within the range of from 350° F. to 700° F.; admixing said heated first pebbles and said petroleum coated second pebbles in said reaction zone; removing said pebbles from the lower portion of said reaction zone; and returning a first portion of said pebbles to the upper portion of said pebble heating zone

7. A heavy oil cracking system comprising in combination a first closed pebble chamber; first pebble inlet means in the upper portion of said first chamber; gaseous effluent outlet means in the upper portion of said first chamber; heating material inlet means in the lower portion of said first chamber; a second closed pebble chamber below said first chamber; first pebble conduit means extending between the lower portion of said first chamber and the top portion of said second chamber; gaseous effluent outlet means in the upper portion of said second chamber; first pebble outlet means in the lower portion of said second chamber; a third closed pebble chamber; second pebble inlet means in the upper end portion of said third chamber; first oil inlet means in the upper end portion of said third chamber; second pebble outlet means intermediate the ends of said third chamber; second pebble conduit means extending between said pebble outlet means in said third chamber and the top portion of said second chamber; excess oil separation means connected to and sloping in a direction common with said second pebble conduit means; an oil supply system connected to said oil inlet means in said third chamber; first oil conduit means extending between said oil separation means and said oil supply system; a plurality of perforations in the lower portion of a laterally extending section of said first pebble outlet means, said perforations having a lateral dimension in the range of from $\frac{3}{16}$ inch to $\frac{5}{16}$ inch; a pebble collector chamber enclosing the lower side of said perforate section of said second pebble outlet means; third pebble outlet means in the lower portion of said pebble collector chamber; and elevator extending between said first pebble outlet means and said first pebble inlet means; a fourth closed pebble chamber above said third chamber; third pebble inlet means in the upper portion of said fourth chamber; an elevator extending between said third pebble outlet means and said third pebble inlet means; a gaseous effluent outlet in the upper portion of said fourth chamber; a gaseous material inlet conduit in the lower portion of said fourth chamber; a fifth closed pebble chamber below said fourth chamber; a pebble conduit extending between the lower portion of said fourth chamber and the upper portion of said fifth chamber; third pebble conduit means extending between the lower portion of said fifth chamber and said second pebble inlet means; a gaseous material inlet in the lower portion of said fifth chamber; and a gaseous material conduit extending between the upper portion of said fifth chamber and said heating material inlet means in said first chamber.

8. The heavy oil cracking system of claim 7, wherein said first pebble conduit means and said second pebble conduit means form a common pebble inlet to said second chamber.

9. The heavy oil cracking system of claim 8, wherein an auxiliary oil inlet is provided in the upper portion of said second chamber and adjacent the outlet of said first pebble conduit means; and second oil conduit means extending between said oil supply system and said second oil outlet means.

10. The heavy oil cracking system of claim 7, wherein a baffle member, smaller in diameter than the inner diameter of said first pebble conduit means, is positioned in that conduit means; and said second pebble conduit means extends from the pebble outlet means in said third chamber to a place in said first conduit means directly over said baffle.

11. The heavy oil cracking system of claim 7, wherein said excess oil separation means comprises a perforate pebble support member forming the bottom closure of said third chamber, and a collector chamber enclosing the lower portion of said perforate pebble support member; and said second pebble conduit means extending from said third chamber at a point adjacent the top surface of said perforate pebble support member.

12. A method for converting a heavy petroleum fraction having an API gravity within the range

of 15 to 20, to lighter hydrocarbon materials which comprises in combination the steps of passing a first portion of pebbles into the upper portion of a pebble heating zone; passing a hot gaseous heating material through said heating zone so as to raise said first pebbles to a temperature within the range of from 2500° F. to 3000° F.; removing gaseous effluent material from said pebble heating zone; passing said first pebbles into the upper portion of a reaction zone and downwardly therethrough; passing a second portion of pebbles into the upper portion of a contact zone and downwardly therethrough; introducing said heavy petroleum into the upper portion of said contact zone; passing said heavy petroleum downwardly through said contact zone in direct contact with said second pebbles, thereby coating said second pebbles with said petroleum; separating said petroleum-coated second pebbles and excess petroleum; returning said excess petroleum to the upper portion of said contact zone; passing said petroleum-coated second pebbles from said contact zone into said reaction zone at a temperature within the range of from 350° F. to 700° F.; admixing said heated first pebbles and said petroleum-coated second pebbles in said reaction zone; removing said pebbles from the lower portion of said reaction zone; returning a first portion of said pebbles to the upper portion of said pebble heating zone; passing the balance of said pebbles into the upper portion of a regeneration zone and downwardly therethrough; passing air into the lower portion of said regeneration zone and upwardly therethrough countercurrent to the flow of pebbles therethrough; oxidizing any carbonaceous deposits on said pebbles in said regeneration zone; removing gaseous effluent from said regeneration zone; passing said pebbles from the lower portion of said regeneration zone into the upper portion of a gas heating zone and downwardly therethrough; passing air through said gas heating zone in direct heat exchange with said pebbles therein, whereby said air is heated and said pebbles are cooled; passing said cooled pebbles into the upper portion of said contact zone; removing said heated air from said gas heating zone; passing said heated air and a combustible fuel to a combustion zone; burning said fuel in said combustion zone; and introducing resulting hot combustion gases into the lower portion of said pebbles heating zone as said hot gaseous heating material.

13. A heavy oil cracking system comprising in combination a first closed pebble chamber; first pebble inlet means in the upper portion of said chamber; gaseous effluent outlet means in the upper portion of said first chamber; heating material inlet means in the lower portion of said first chamber; a second closed pebble chamber below said first chamber; first pebble conduit means extending between the lower portion of said first chamber and the top portion of said second chamber; gaseous effluent outlet means in the upper portion of said second chamber; pebble outlet means in the lower portion of said second chamber; a third closed pebble chamber above said second chamber; pebble inlet means in the upper end portion of said third chamber; first oil inlet means in the upper end portion of said third chamber; pebble outlet means in the lower portion of said third chamber; second pebble conduit means extending downwardly between said pebble outlet means in said third chamber and the top portion of said second chamber; excess oil separation means comprising a perforate pebble support member forming the bottom closure of said third chamber, and a collector chamber enclosing the lower portion of said perforate pebble support member, connected to and sloping in a direction common with said second pebble conduit means, said second pebble conduit means extending from said third chamber at a point adjacent to the top surface of said perforate support member; an oil supply system connected to said oil inlet means in said third chamber; first oil conduit means extending between said oil separation means and said oil supply system; and a pebble transfer means extending between said pebble outlet means in said second chamber and said pebble inlet means in said first and third chambers.

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