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 PEBBLE HEATING APPARATUS FOR CARRYING OUT
 A PLURALITY OF PROCESSES CONCOMITANTLY
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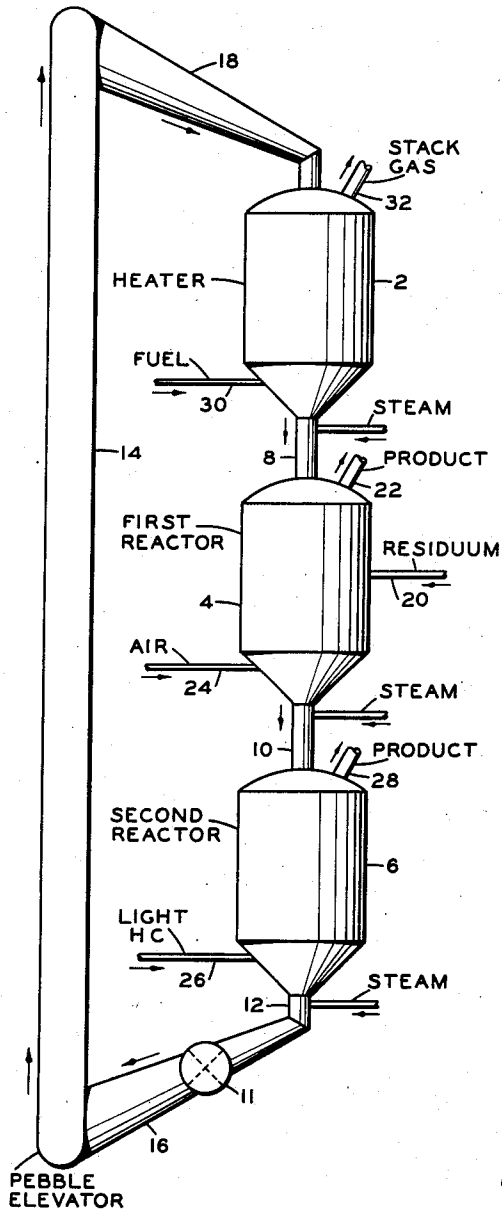


FIG. 1

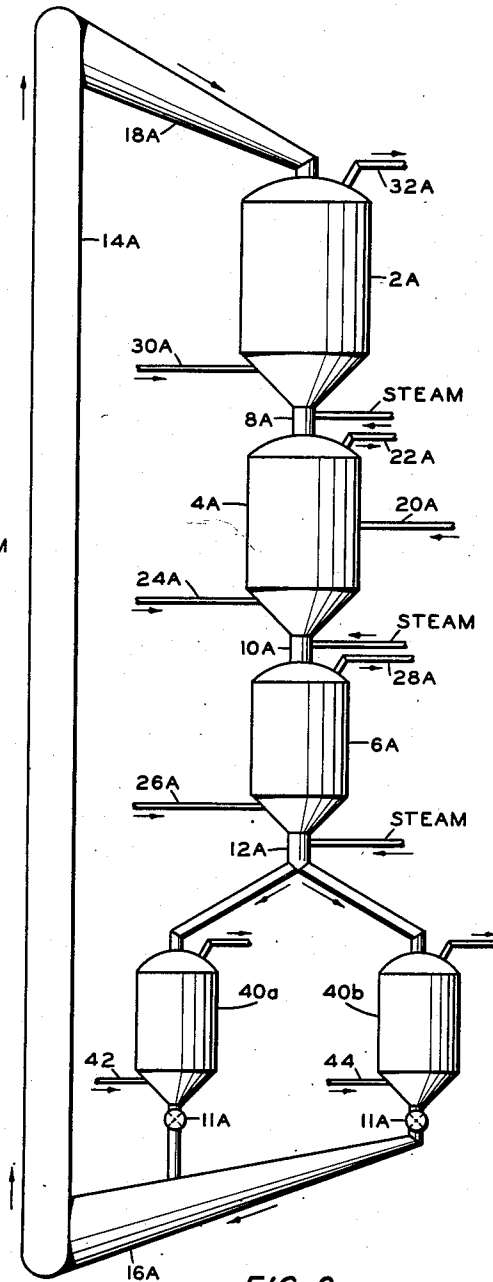


FIG. 2

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PEBBLE HEATING APPARATUS FOR CARRY-
ING OUT A PLURALITY OF PROCESSES
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This invention relates to methods and apparatus for heating hydrocarbons to high temperatures.

A particular embodiment of the invention relates to a method and an apparatus for the concomitant pyrolysis of a heavy hydrocarbon and another lighter, more refractory, hydrocarbon by contacting said hydrocarbons with a stream of hot pebbles.

In hydrocarbon conversion processes which require high temperatures and which are endothermic in character, such as thermal cracking and thermal dehydrogenation, pebble-heater-type apparatus functions most satisfactorily. The pebble heater method entails the heating of refractory "pebbles" in a heating chamber by the combustion of fuel gases and the transference of the resulting hot pebbles to a second heating or conversion chamber for heating the gases being processed and furnishing the heat of reaction. A continuous stream of hot pebbles is passed through the conversion chamber by gravity flow and transferred by means of a bucket-type elevator (or other lifting device) to the pebble heater for reheating and recycling through the system.

One difficulty which arises when heavy hydrocarbons, say heavy residuum, are cracked in pebble heaters is the accompanying coke and carbon deposition on the pebbles which causes plugging at the cracking chamber outlet constricting the flow of pebbles therethrough.

In the cracking of light hydrocarbons, say propane, pebble heaters function more advantageously, but heretofore pebbles leaving the cracking chamber outlet were at a very high temperature and could be handled in elevator equipment only if high temperature alloy materials were used in its construction.

Another inherent limitation of pebble heater operation is that for a given process a large portion of the pebble heat is lost through recirculation of the high temperature pebbles. In a given plant where two or more heaters are employed for the same or different processes these heat losses are thereby multiplied.

An object of the present invention is to inhibit plugging in pebble reactors due to coke and carbon deposition.

Another object of the invention is to provide a process and apparatus for the concomitant pyrolysis of heavy hydrocarbon and a more refractory lighter hydrocarbon.

A further object of this invention is to provide improvements in pebble heating apparatus for conversion of hydrocarbon gases.

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Other objects and applications of the present invention will become apparent from the accompanying description.

In one embodiment of the instant invention a process is provided for concomitantly cracking heavy hydrocarbons and light refractory hydrocarbons which comprises heating a gravitating compact column of refractory pebbles in an upper confined heating chamber by contact with hot combustion gas; gravitating the resulting hot pebbles through a relatively narrow passageway into a first expanded reaction chamber; contacting the gravitating column of pebbles in the upper section of said reaction chamber with a heavy hydrocarbon under cracking conditions; removing carbon deposited on the pebbles during the cracking operation by surface combustion with air introduced in the lower section of the first reaction chamber forming a well defined combustion zone, withdrawing cracked products plus inert products of combustion at the top of said first reaction chamber; gravitating the hot pebbles resulting from surface combustion in the first reaction chamber through a relatively narrow passageway into a second expanded reaction chamber; contacting the gravitating column of pebbles in the second reaction chamber with light refractory hydrocarbons under cracking conditions, and recovering the products.

By a heavy hydrocarbon I mean, of course, a hydrocarbon at least as heavy as gas oil. This includes petroleum hydrocarbons obtained by the distillation of crude petroleum, for example fuel oil, refinery gas oil and reduced crude, as well as cracked residuum etc. By a more refractory hydrocarbon I mean a hydrocarbon lighter than gas oil. Particularly suitable refractory hydrocarbons are butane, propane and the like. The hydrocarbons employed in any particular instance will be obvious given the accompanying disclosure of my invention.

The term "pebble" as used throughout the specification denotes any refractory material in flowable form and size which can be utilized to carry heat from one zone to another. Pebbles are conventionally substantially spherical and are from about $\frac{1}{8}$ " to about 1" in diameter with the preferred size for high temperature processes about $\frac{1}{4}$ ". Pebbles must be of refractory materials which will withstand temperatures at least as high as the highest temperature attained in the pebble heating zone. Pebbles which will withstand temperatures in the range of about 3500° to 4000° F. are now in use.

Pebbles compacted from ceramic material such as alumina, mullite, zirconia, thoria, periclase,

synthetic and natural clays function advantageously. Pebbles may be either catalytic or inert with respect to the pyrolytic process.

For a more complete understanding of the invention reference may be had to the accompanying drawing in which Figure 1 is a diagrammatic showing of my apparatus arranged for the heating of pebbles and the pyrolysis of two different hydrocarbons.

Figure 2 is a diagrammatic sketch of a similar arrangement showing a different embodiment of the instant invention.

In Figure 1 reference numeral 2 is an insulated refractory lined heating chamber for heating flowing pebbles of a ceramic or metallic composition; numerals 4 and 6 designate heating chambers of similar construction for cracking hydrocarbons, the former being adapted as described hereinafter for burning carbon and coke from the pebbles; and 14 is an elevator of the continuous, bucket type, for transferring pebbles from chamber 6 to chamber 2 for reheating and recycling through the system. Chambers 2, 4 and 6 are arranged at successively lower levels and are connected by conduits 8 and 10 to accommodate the natural flow of pebbles through the apparatus. A star wheel 11, or other pebble feeding device, in conduit 12 controls the rate of flow of pebbles through the apparatus and feeds the pebbles to conduit 16 leading to elevator 14. A proper screening device can be inserted in conduit 16 for removing fines and broken pebbles through a closable opening (not shown). Pebbles reaching the top of elevator 14 are dumped into conduit 18 from which they flow into heating chamber 2 for reheating and recycling. Conduit 18 is provided with means (not shown) for introducing fresh pebbles to the system. Steam lines are provided in connecting conduits 8, 10 and 12 for admitting sufficient steam to the connecting conduits to prevent any substantial escape of gas from one chamber to another wherein substantially equal pressures are maintained; these pressures being subatmospheric, atmospheric, or superatmospheric as desired.

The heavy hydrocarbon, e. g. residuum is introduced to heating chamber 4 through line 20 in the upper section, i. e. at the midpoint of chamber 4 or above, and the product is removed through line 22. Another line 24 is provided in the lower section of chamber 4 for admitting air to the chamber for removing coke and carbon from pebbles by surface combustion before the pebbles pass through conduit 10. The combustion gases from this section assist in stripping the cracked residuum products which are removed at the top at 22 of chamber 4. A second reactor 6 below the first utilizes the heat in the pebbles from surface combustion in the first reactor 4 to carry out a heating or cracking operation in chamber 6, such as cracking a light hydrocarbon, e. g. ethane or propane, or superheating steam or air. The gas to be heated or cracked is admitted to reactor 6 through line 26 and the product is removed through line 28. In pebble heater 2 fuel and air are fed through line 30 and combustion gas or flue gas passes out through line 32.

Figure 2 shows another embodiment of this invention. In addition to the three chambers 2A, 4A and 6A, which are similar to 2, 4 and 6 in Figure 1, chambers 40a and 40b are interposed before elevator 14A. Chambers 40a and 40b are waste heat boilers having one or more lines such as 42 and 44 for preheating all of the air and/or

fuel for the combustion section 2A, as well as the hydrocarbon feeds to 4A and 6A.

As indicated this apparatus is particularly advantageous for concomitantly cracking residuum and propane. Specific details relating to the cracking of residuum and propane by pebble heater operation are well known to those skilled in the art and do not form a part of this invention. In general, residuum is ordinarily cracked at a temperature of from 1100° F. to 1400° F. The pebble ratio in such cases is usually from 15 to 30 pounds per pound of hydrocarbon feed, and residence time is estimated to be generally about one second. For a fuel oil produced by vacuum distillation boiling below 900° F. and having an API gravity of 15.8, and a viscosity SUV at 210° F. of 730 and converted in a pebble reactor, the per cent conversion to normally gaseous products ranges from 15 per cent at 1170° F. to 50 per cent at 1350° F. At a 40 weight per cent conversion to normally gaseous products 100 pounds of residuum cracked in such a heating apparatus will yield about 17 pounds of gasoline, and, of course lay down coke which is burned off as disclosed herein.

Propane is generally cracked at temperatures in the range of from 1450° F. to 1800° F., the residence time being usually from 0.01 second to 0.1 second. In a pebble heater reactor such as described herein at 1750° F. the pebble rate is usually about 61,200 pounds per hour with a feed rate of about 11,700 pounds per hour.

In operation refractory pebbles fill the three heating chambers 2, 4 and 6, and the connecting conduits, their flow through the system being regulated by the operation of star wheel 11 (11A in Figure 2) in conduit 12 according to the temperature required in conversion chamber or reactor 4. Since the feed to reactor 6 can be increased to whatever rate is needed to use up heat from the combustion of carbon on the pebbles in reactor 4, the temperature of the pebbles flowing to the elevator can be kept relatively cool. Pebbles are heated in chamber 2 by combustion gases flowing therethrough from any conventional source through line 30. The rate of combustion and the degree of preheating of the air and/or fuel entering pebble heater 2 determine the temperature attained in the heater. Combustion gases withdrawn through line 32 can be utilized in any desirable manner to recover the sensible heat thereof. Heated pebbles are permitted to flow through line 8 to chamber 4 at a rate and temperature which insure the maintenance of the desired conversion temperature in the upper section of reactor 4. The higher the temperature differential between pebble temperature and conversion temperature the slower will be the rate of flow and vice versa. In chamber 4 residuum to be cracked enters line 20 and products are withdrawn through line 22. In the bottom section of reactor 4 air entering at line 24 is used to burn carbon or coke laid down on the pebbles entering the cracking operation in the upper section of pebble reactor 4. Inert products of combustion leave reactor 4 at 22 along with the product. By burning off the carbon laid down on the pebbles a well defined combustion zone is formed in the bottom section of reactor 4. Excess or secondary air can be used but only the theoretical amount of air need be employed. To assist in defining the afore-mentioned zone and, if desired, to raise the temperature, air and fuel, e. g. natural gas, can be introduced in stoichio-

metric ratio to burn completely to water, or steam, and carbon dioxide. Besides removing carbon to prevent plugging conduit 10 this combustion operation has the further advantage that the combustion gases from this section assist in stripping the cracked residuum products which are removed at the top 22 of the first reactor. Hot pebbles flowing from the bottom of reactor 4 through conduit 19 provide heat for the pyrolysis of propane or some other lighter more refractory hydrocarbons, with the feed rate being adjusted as indicated hereinbefore to whatever rate is needed to use up heat from the combustion of carbon on the pebbles.

It can be seen that by this invention two or more pebble reactors can be combined to produce a greatly improved process through the provision for surface combustion in the first pebble reactor. By the process of the instant invention instead of multiplying heat losses as is the case when two separate pebble reactors are in operation substantially all of the heat from pebbles is utilized with a minimum of heat loss. Moreover the desired features of surface combustion are provided in the first pebble reactor in accordance with the practice of this invention. Air can be added in controlled quantity for the combustion of coke from the pebbles approaching the flame localization area, and surface combustion is complete without the use of secondary or excess air. My invention is extremely advantageous in the alleviation of plugging in the neck of the pebble reactor. An additional advantage is that the combustion gases assist in stripping as noted hereinbefore. This plugging due to carbon and coke deposition has been a problem of considerable concern in the cracking of heavy hydrocarbons in pebble heater reactors. Finally this invention accomplishes, among other things, what would be obtained if the pebbles passed downward from one reactor into a second pebble heater, or back to the first pebble heater, and from the second pebble heater to a second reactor but without plugging due to carbon deposition and with increased efficiency due to degree of completion.

The above description with respect to the drawings is intended to be illustrative of the invention only and many different embodiments may be made without departing from the spirit and scope thereof.

I claim:

1. A process for concomitantly cracking a heavy residuum and propane which comprises heating a gravitating compact column of refractory pebbles in an upper confined heating chamber by contact with hot combustion gas; gravitating the resulting hot pebbles through a relatively narrow passageway into a first expanded reaction chamber; contacting the gravitating column of pebbles in the upper section of said reaction chamber with a heavy residuum under cracking conditions; removing carbon deposited on the pebbles during the cracking operation by surface combustion with air introduced in the lower section of the first reaction chamber, withdrawing cracked products plus inert products of combustion at the top of said first reaction chamber; gravitating the hot pebbles resulting from surface combustion through a relatively narrow passageway into a second expanded reaction chamber; and contacting the gravitating column of pebbles in the second reaction chamber with propane under cracking conditions,

2. A process for concomitantly cracking a heavy residuum and propane which comprises heating a gravitating compact column of refractory pebbles in an upper confined heating chamber by contact with hot combustion gas; gravitating the resulting hot pebbles through a relatively narrow passageway into a first expanded reaction chamber; contacting the gravitating column of pebbles in the upper section of said reaction chamber with a heavy residuum under cracking conditions; removing carbon deposited on the pebbles during the cracking operation by surface combustion with air introduced in the lower section of the first reaction chamber, withdrawing cracked products plus inert products of combustion at the top of said first reaction chamber; gravitating the hot pebbles resulting from surface combustion through a relatively narrow passageway into a second expanded reaction chamber; contacting the gravitating column of pebbles in the second reaction chamber with propane under cracking conditions; and adjusting the feed rate of propane into said reaction chamber at the rate necessary to use up pebble heat resulting from the previous combustion of carbon on the pebbles.

3. A process for concomitantly cracking a heavy residuum and propane which comprises in a system in which three superposed chambers are employed in series, heating pebbles in the first chamber to a temperature above the cracking temperature to be used in the second chamber, passing the heated pebbles to the top of said second chamber to provide heat for cracking in said chamber, subjecting a residuum to cracking conditions in the upper section of said second chamber, by surface combustion in the lower section of said second chamber removing the coke and carbon deposited on the pebbles during cracking in the upper section of the second chamber, passing the hot pebbles from said combustion in the lower section of the second chamber to the third chamber to provide heat for cracking in said third chamber and cracking propane in said third heating chamber.

4. A process for concomitantly cracking a highly refractory material and a less refractory material which comprises in a system in which three chambers in vertical alignment are employed, heating a gravitating compact column of refractory pebbles in the upper chamber, gravitating the hot pebbles from said upper chamber into the middle chamber, contacting the gravitating column of pebbles in the upper section of said middle chamber under cracking conditions with a hydrocarbon at least as heavy as gas oil, removing carbon deposited during said cracking operation by surface combustion in the lower section of said middle chamber, gravitating into the lower chamber the hot pebbles resulting from surface combustion in the middle chamber, and contacting the gravitating column of pebbles in said lower chamber under cracking conditions with a hydrocarbon at least as refractory as butane.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,194,574	Snyder	Mar. 26, 1940
2,362,621	Fahnestock	Nov. 14, 1944
2,426,848	Tuttle	Sept. 2, 1947
2,432,520	Ferro	Dec. 16, 1947
2,486,627	Arnold	Nov. 1, 1949
2,514,497	Jones	July 11, 1950
2,532,613	Dutcher	Dec. 5, 1950
2,582,016	Dutcher	Jan. 8, 1952