

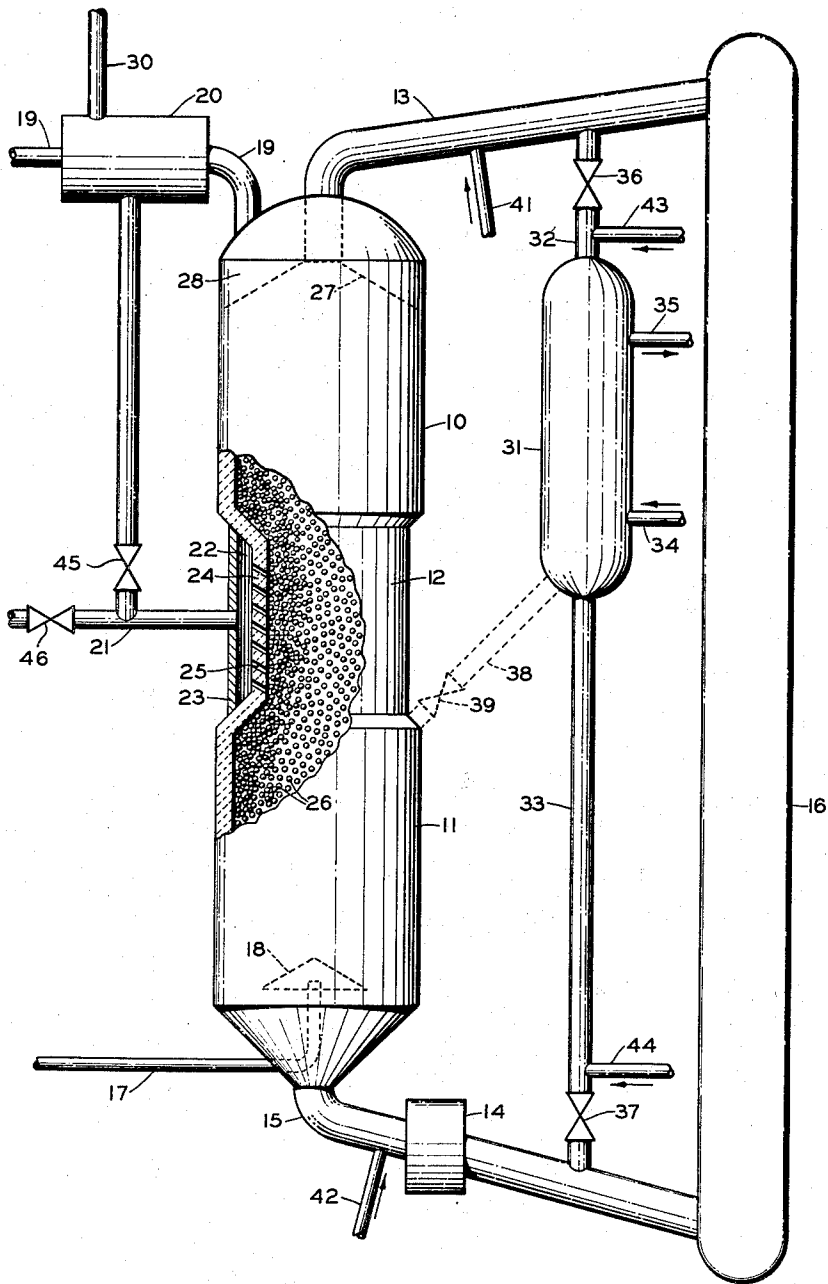
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PEBBLE HEAT EXCHANGE CONVERSION PROCESS

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PEBBLE HEAT EXCHANGE CONVERSION
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This invention relates to a process and apparatus for the thermal conversion of hydrocarbons utilizing pebble heat-exchange. A specific aspect of the invention pertains to the cracking of light hydrocarbons to less saturated hydrocarbons by pebble-heat exchange.

Conventional pebble heat-exchange processes entail gravitating a contiguous compact stream of pebbles thru an upper chamber in contact with hot combustion gas and then gravitating the hot pebbles thru one or more relatively narrow pebble passageways to a lower pebble heat-exchange chamber where the hot pebbles are utilized to heat a suitable feed gas, such as a hydrocarbon, in countercurrent flow. In order to make it feasible to withdraw the reaction product or treated gas from the upper portion of the lower heat-exchange chamber the connecting pebble passageway (or throat) is extended into the lower chamber a short distance so as to provide a gas collecting or vapor space above the pebble bed for collection and withdrawal of the gas thru one or more communicating conduits. It has been found that when effecting hydrocarbon conversion processes at high temperatures in this type of apparatus it is difficult if not impossible to avoid coke formation and deposition in the vapor space above the pebble bed in the lower chamber. Coke formation is caused by the overcracking of the hydrocarbon being treated due to "soaking" of the hydrocarbon or products of the conversion in the vapor space, which condition is aggravated by the difficulty of rapidly withdrawing the hydrocarbon effluent from the upper portion of the reactor. The copending application of M. O. Kilpatrick and H. J. Hepp, Serial No. 699,666, filed September 27, 1946, now Patent No. 2,559,957 is concerned with the avoidance of carbon deposition in the upper portion of a pebble heater reactor and offers one solution to this problem. The invention there is in the design of the reactor which eliminates the projection of the pebble throat into the upper portion of the reactor by disposing the throat at the periphery of the reactor and streamlining the flow of hydrocarbon from the top of the pebble bed thru a gradually converging top closure member into a gas take-off.

The present invention is concerned primarily with the elimination of carbon deposition in the upper portion of the lower pebble heat-exchange chamber of a pebble heat-exchanger apparatus.

The principal object of the invention is to provide a pebble heat-exchange process and apparatus for the thermal conversion of hydrocarbons which prevents coke formation on the walls and

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throat in the upper portion of the lower pebble heat-exchange chamber of a two-chamber pebble heater apparatus. It is also an object of the invention to provide an economical and thermally efficient pebble heat-exchange process and apparatus for the conversion of hydrocarbons. Another object is to provide an improved process for cracking light hydrocarbons, including propane, ethane, and methane to less saturated hydrocarbons, such as propylene, ethylene, and acetylene; and for cracking ethylene and/or propylene with or without admixed acetylene to butadiene, cyclopentadiene, and aromatics. A further object of the invention is to provide an improved process for cracking methane to acetylene and aromatic oils. Other objects of the invention will become apparent from a consideration of the accompanying disclosure.

The invention eliminates the gas collecting or vapor space in the upper portion of the lower chamber of a two-chamber pebble heater apparatus by sloping the top closure member and refractory lining at an angle with the horizontal greater than the angle of repose of the pebbles used in the process. This sloping top closure member joins the throat or pebble passageway connecting the two heat-exchange chambers in such a manner as to avoid the formation of a vapor space between the pebble bed and the refractory walls of the apparatus, thereby preventing the formation of carbonaceous deposit in this area when the apparatus is being used in the high temperature conversion of hydrocarbons. This structure is made possible by the elimination of the necessity for withdrawal of gas or vapor from the upper portion of the lower heat-exchange chamber. Instead the hydrocarbon being treated is passed upwardly thru the pebble throat which also serves as a combustion chamber to which a regulated amount of oxygen-containing gas, such as air or pure oxygen, is introduced so as to burn a sufficient portion of the hydrocarbon to supply the heat necessary to effect the desired conversion of the hydrocarbon in the pebble heat-exchanger system. Hydrocarbon conversion is effected in the pebble passageway-combustion chamber between the pebble heat-exchange chambers and continues in the lower portion of the upper chamber. Heat-exchange between the hot reaction products and the cooler pebbles takes place in the upper portion of the upper heat-exchanger so as to recover heat from the reaction effluent and render the process more thermally efficient.

Pebbles utilized in the process of the invention are preferably small spheres ranging in diameter

from $\frac{3}{16}$ " to $1\frac{1}{2}$ " compacted from alumina, mullite, alumina-mullite, magnesite, zirconia, thoria, periclase, Monel, inconel, and similar highly refractory materials. The ceramic materials used in manufacturing pebbles must be heat treated at high temperature so as to bond and glaze the pebbles to make them more rugged and attrition resistant in gravitating heat-exchange operation. Non-spherical pebbles are generally economically impractical because of the excessive attrition losses suffered in gravitating bed processes. Pebbles, particularly of alumina and mullite, have been developed which withstand temperatures above 3000° F. and which suffer very little attrition loss.

For a more complete understanding of the invention, reference is made to the drawing which is a plan view, partly in section, of a preferred modification of the invention.

Pebble heat-exchangers 10 and 11 in connecting throat or pebble passageway 12 are vertically aligned to facilitate the gravitation of a compact contiguous stream of pebbles thru the apparatus from pebble inlet conduit 13 to pebble feeder or flow regulator 14 in pebble chute 15 leading to elevator 16. Pebble feeder 14 may be any suitable device, such as a table feeder, star valve, or a vibrating screen type feeder which is regulable so as to control the flow of pebbles thru the unit. Elevator 16 may be of the bucket, screw, or gas lift type. Line 17 is a feed line to the lower portion of chamber 11 and delivers feed gas to a suitable gas distributing means 18. Line 19 is a take-off line for the effluent from the process, while line 21 serves to introduce an oxygen-containing gas to the interior of throat 12 thru the annular gas space 22 formed by concentric cylindrical refractories 23 and 24. The downwardly and inwardly sloping openings or slots 25 distributed uniformly at short intervals around the refractory wall 24 serve to conduct oxygen-containing gas from annular space 22 to the pebble stream 26 in the interior of throat 12 without admitting pebbles to annular space 22. While lines 17, 19, and 21 are shown as single lines, a plurality of lines may be utilized to perform their function. Pebble chute 13 extends into the upper portion of chamber 10 a substantial distance so as to form a pebble bed having a top surface indicated at 27, thereby forming a gas collection or vapor space 28 above the pebble bed.

Chamber 31 connected with pebble chutes 13 and 15 by pebble conduits 32 and 33, respectively, is a pebble regeneration chamber which is utilized for burning off the carbon deposited on the pebbles during their passage thru pebble chambers 10, 11, and 12. Lines 34 and 35 serve to pass oxygen-containing gas to and withdraw combustion gas from chamber 31. Flow control valves 36 and 37 serve to regulate the rate of flow of pebbles thru regeneration chamber 31. Pebble conduit 38 and valve 39 provide an alternative flow of pebbles from regeneration chamber 31 into the system thru the upper portion of chamber 11.

Lines 41, 42, 43, and 44 serve to introduce steam or other blocking gas to confine the hydrocarbon to the treating zones.

In operation a suitable hydrocarbon feed, usually in gas or vapor form, is introduced into the lower portion of chamber 11 thru line 17 where it is distributed by gas distribution means 18 for uniform flow upwardly thru heat-exchanger 11 in countercurrent flow to a gravitating stream of pebbles which have been heated

by combustion of a portion of the hydrocarbon in pebble passageway-combustion chamber 12 and in the lower portion of the upper heat-exchanger 10. The hydrocarbon is preferably heated to approximately the temperature at which conversion, such as cracking, takes place. By the time it reaches the entrance to the combustion chamber, air or other oxygen-containing gas introduced thru line 21 and distributed thru gas space 22 passes thru slots 25 at relatively high velocity into the void spaces of the gravitating contiguous, compact stream of pebbles 26 in the combustion chamber and burns a suitable portion of the hydrocarbon ascending this passageway. Sufficient hydrocarbon is burned to supply the endothermic heat of reaction required and to make up for the loss of heat thru radiation and in the effluent take-off thru line 19. If the hydrocarbon is not preheated to reaction temperature on its ascent thru pebble-heat exchanger 11, sufficient heat must also be provided by combustion to raise the temperature of the hydrocarbon to reaction temperature. The conversion initiated in combustion chamber 12 is continued in the lower portion of conversion heat-exchanger 10 until the reaction is stopped by contact with cool pebbles descending chamber 10.

It is desired to control the process so that the effluent passing out thru line 19 is reduced to a temperature below 1000° F., and preferably below 800° F., so as to increase the thermal efficiency of the apparatus and process. Likewise, it is desirable to cool the pebbles descending heat-exchanger 11 to a temperature below 1000° F. and preferably below 800° F. By maintaining a low pebble exit temperature at the bottom of pebble heat exchanger 11, heat losses in the pebble conduits and elevator between the pebble outlet from chamber 11 and the pebble inlet to chamber 19 are kept to a minimum. This method of operation also permits the use of ordinary cast iron or steel equipment in this part of the apparatus and thereby substantially reduces the cost and maintenance of equipment.

Outlet pebble and gas temperatures may be controlled in part by the depth of the pebble beds in chambers 10 and 11. In general, the deeper the pebble bed the more complete the heat exchange and the lower the ultimate temperature differential between pebbles and gas. However, the length of chambers 10 and 11 should not be so great as to effect an undesirable pressure drop thru the gravitating pebble bed. It is obvious that the maintenance of a low pebble outlet temperature from heat-exchanger 11 aids in maintaining a low gas temperature in line 19 in any given unit.

In the conversion of hydrocarbons, especially involving cracking, in pebble heat-exchange apparatus such as that shown in the drawing, when operated according to the invention carbonaceous material is deposited on the pebbles in the upper portion of heat-exchanger 11, in combustion chamber 12, and in the lower portion of heat-exchanger 10. In order to maintain the pebbles sufficiently free of carbon for efficient heat-exchange and to avoid agglomeration of the pebbles, the invention provides for the withdrawal of a portion of the pebbles during each cycle thru valve 36 so as to pass the pebbles in a contiguous stream thru line 32, regeneration chamber 31, and line 33 back to pebble chute 15. In regeneration chamber 31 the carbon coated pebbles are contacted with a stream of oxygen-containing gas admitted thru line 34 under suit-

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able conditions for burning off the carbon from the pebbles. In this manner, by removing a certain fraction of the pebble stream passing thru conduit 13, removing at least a substantial portion of the carbon therefrom, and returning them to the pebble stream passing thru the system, the main pebble stream is kept sufficiently free of carbon to permit efficient use of the pebbles as heat-exchange material in the process. If the pebbles entering regeneration chamber 31 are too cool to support combustion when contacted with air at atmospheric temperature, the air admitted thru line 34 may be preheated to any required temperature. On the other hand, in some cases it might be necessary to dilute the oxygen-containing gas so as to maintain sufficiently low oxygen content to avoid overheating of the pebbles. In some cases the pebbles passing out the bottom of chamber 31 are too hot to pass directly into pebble chute 15 thru line 33 and valve 37 and it is advantageous to pass them into the upper portion of chamber 11 thru line 38 and valve 39 so as to utilize their heat content in chamber 11 to preheat the hydrocarbon feed and cool them to suitable transfer temperature.

In one modification of the invention in order to reduce dilution of the product stream with combustion gas and to improve the thermal efficiency of the process, valves 45 and 46 are operated so that the air for combustion in combustion chamber 12 is passed thru line 30 and heat-exchanger 20 in indirect heat-exchange with the hot effluent in line 19. This expedient further increases the thermal efficiency of the process by reducing the heat loss in the effluent in line 19. In some cases it may be desirable to use a water quench in line 19.

The process may be operated at any suitable pressure, but pressures just above atmospheric pressure are preferred. Lines 41, 42, 43, and 44 are utilized for admitting steam or other blocking gas to the pebble conduits to confine the gasses in main unit and in regeneration chamber 31.

When converting propane and/or other lower boiling hydrocarbon, it may be desirable in some instances to admit hot combustion gas thru line 21 in order to conserve the more valuable hydrocarbon being converted. Excess air or oxygen may be used, thereby furnishing a further portion of reaction heat by oxidation of the feed stock by the residual oxygen. This method of operation permits the use of less expensive fuel gas for furnishing heat or reaction and other heat requirements of the process.

The following example illustrates the invention in the cracking of ethane to produce ethylene.

Example

Ethane feed amounting to 138,000 C. F. H. (10,910 pounds) is introduced thru line 17 and flows upwardly thru preheater 11 countercurrent to a gravitating stream of $\frac{3}{8}$ " alumina pebbles which are circulated at an approximate rate of 50,000 pounds per hour. Chamber 11 has an approximate internal diameter of 5' and a pebble bed depth of 7'. The upper portion of this chamber is sloped or shaped so as to avoid any open space between the walls and the pebbles. The outgoing pebbles from preheater 11 are cooled to about 700° F. while the ethane is preheated during its ascent thru the chamber to about 1700° F. The preheated ethane is quickly mixed in

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throat 12 with 167,000 C. F. H. of combustion air preheated to a temperature of 700° F.

Reaction occurs in the throat or combustion chamber and in the lower part of conversion chamber 10, the hot cracked products being rapidly cooled by contact with cool pebbles in the higher regions of chamber 10 which is sized with due regard to pebble-lifting gas velocities and heat transfer rates, in the present case being 6' internal diameter and providing a pebble bed depth of about 6'. The cracked effluent from chamber 10 has a temperature of about 800° F. and is further cooled in heat-exchanger 20 to below 500° F. Only a negligible amount of carbon is deposited on the upper walls of chamber 11. The effluent has the following composition:

	C. F. H.	Percent (Dry Basis)
H ₂	69,600	19.6
CH ₄	8,040	2.3
C ₂ H ₆	1,400	0.4
C ₂ H ₄	67,500	19.0
C ₂ H ₂	47,700	13.4
C ₃ H ₈	1,530	0.4
CO.....	24,000	6.8
CO ₂	2,700	0.8
N ₂	132,000	37.3
Steam.....	40,000	-----
	394,470	100.0

The product effluent may be worked up in any desired manner for recovering valuable constituents by methods known in the art and the ethylene recovered by a low temperature fractionation. Ethane is desirably recycled to the process.

As a further modification of the invention, oxygen may be introduced thru line 21 in place of air and will eliminate the nitrogen diluent in the reaction products, thus reducing dilution and making it easier to recover ethylene and also hydrogen.

The example merely illustrates one type of process for which the invention is particularly suited and is not to be interpreted as unduly and unnecessarily limiting the invention. The invention is applicable to the endothermic conversion of hydrocarbons broadly. It has particular utility in the cracking of low molecular weight paraffins and olefins, either singly or in admixture, so as to produce olefins, diolefins, acetylene, aromatics, etc.

I claim:

1. A process for endothermic conversion of a hydrocarbon, comprising gravitating a contiguous compact stream of hot pebbles thru a series of contiguous zones including an upper conversion zone, a lower feed preheating zone, and an interconnecting combustion zone; contacting that section of said pebble stream in said preheating zone with an ascending stream of convertible hydrocarbon so as to preheat same; passing the entire preheated hydrocarbon stream directly thru said interconnecting combustion zone in contact with said pebble stream; burning a sufficient portion of said preheated hydrocarbon stream by introducing oxygen-containing gas into said interconnecting combustion zone into admixture with the hydrocarbon therein to further heat and to effect desired conversion of said hydrocarbon with concomitant heating of the pebbles in said interconnecting combustion zone and in the lower portion of said conversion zone; and passing the entire effluent from said interconnecting combustion zone into said conversion zone and continuing the

conversion in the lower portion of said conversion zone; transferring pebbles from the lower portion of said preheating zone to the upper portion of said conversion zone; and recovering a converted hydrocarbon effluent from said conversion zone.

2. A process for endothermic conversion of a hydrocarbon, comprising gravitating a contiguous compact stream of hot pebbles thru a series of contiguous zones including an upper conversion zone, a lower feed preheating zone, and an interconnecting combustion zone; contacting that section of said pebble stream in said preheating zone with an ascending stream of convertible hydrocarbon so as to preheat same; maintaining the upper portion of said preheating zone full of pebbles so as to avoid stagnant gas spaces with concomitant deposition of carbon therein; passing the entire preheated hydrocarbon stream directly thru said interconnecting combustion zone in contact with said pebble stream; burning a sufficient portion of said preheated hydrocarbon stream by introducing an oxygen-containing gas into said interconnecting combustion zone into admixture with the hydrocarbon therein to further heat and to effect desired conversion of said hydrocarbon with concomitant heating of the pebbles in said interconnecting combustion zone and in the lower portion of said conversion zone; and passing the entire effluent from said interconnecting combustion zone into said conversion zone and continuing the conversion in the lower portion of said conversion zone; transferring pebbles from the lower portion of said preheating zone to the upper portion of said conversion zone; and recovering a converted hydrocarbon effluent from said conversion zone.

3. A process for endothermic conversion of a hydrocarbon, comprising gravitating a contiguous compact stream of hot pebbles thru a series of zones including an upper conversion zone, a lower feed preheating zone, and an interconnecting combustion zone; contacting that section of said pebble stream in said preheating zone with an ascending stream of convertible hydrocarbon so as to preheat same; maintaining the upper portion of said preheating zone full of pebbles so as to avoid stagnant gas spaces with concomitant deposition of carbon therein; passing the preheated hydrocarbon thru said interconnecting zone in contact with said pebble stream; burning a sufficient portion of said preheated hydrocarbon stream by introducing an oxygen-containing gas into said interconnecting zone into admixture with the hydrocarbon therein to further heat and to effect desired conversion of said hydrocarbon with concomitant heating of the pebbles in said interconnecting zone and in the lower portion of said conversion zone; continuing the conversion in the lower portion of said conversion zone whereby carbonaceous material is deposited on the pebbles; transferring pebbles from the lower portion of said preheating zone to the upper portion of said conversion zone; passing a portion of the pebble stream after withdrawal from the lower portion of the preheating zone and before introduction to the conversion zone thru a regeneration zone and there burning off at least a portion of the carbonaceous material from said pebbles with an oxygen-containing gas and returning the regenerated pebbles to said gravitating stream; and recovering a converted hydrocarbon effluent from said conversion zone.

4. The process of claim 3 in which the regenerated pebbles are returned to the conversion zone.

5. The process of claim 3 in which said regenerated pebbles are returned to the preheating zone.

6. The process of claim 2 in which the conversion comprises cracking.

7. The process of claim 2 in which the conversion comprises cracking a light hydrocarbon.

8. The process of claim 2 in which the conversion comprises cracking methane.

9. The process of claim 2 in which the conversion comprises cracking ethane.

10. The process of claim 2 in which the conversion comprises cracking propane.

11. A process for cracking a light hydrocarbon, comprising gravitating a contiguous compact stream of hot pebbles through a series of contiguous zones including an upper cracking zone, a lower feed preheating zone, and an interconnecting combustion zone; passing a light hydrocarbon feed upwardly through said preheating zone in countercurrent contact with said pebbles so as to heat said feed to a temperature in the range of 1000° F. to the incipient cracking temperature of said feed and cool said pebbles to a temperature below 1000° F.; maintaining the upper portion of said preheating zone full of pebbles so as to avoid stagnant gas spaces with concomitant deposition of carbon therein; passing the entire heated feed upwardly through said combustion zone and there burning such a portion of same by admixture with an oxygen-containing gas to heat and crack said feed with concomitant heating of the pebbles in the combustion zone; passing the entire resulting gaseous mixture upwardly through said cracking zone with continued cracking of the hydrocarbon and heating of pebbles in the lower portion thereof and with cooling of the cracked effluent and heating of the pebbles in the upper portion thereof; transferring pebbles from the lower portion of said preheating zone to the upper portion of said cracking zone; and recovering cracked product from the upper portion of said cracking zone.

12. The process of claim 11 in which carbonaceous material is deposited on said pebbles from the cracking step and a portion of the pebble stream is continuously passed through a separate combustion zone in contact with an oxygen-containing gas at combustion temperature so as to burn off at least a portion of said material, and is then returned to said gravitating stream of pebbles.

13. A process for cracking ethane to produce ethylene which comprises gravitating a contiguous compact stream of hot pebbles through a series of contiguous zones including an upper cracking zone, a lower feed preheating zone, and an interconnecting combustion zone; passing an ethane-rich feed upwardly through said preheating zone in countercurrent contact with said pebbles so as to heat said feed to a temperature in the range of 1400 to 1800° F. and cool said pebbles to a temperature below 1000° F.; maintaining the upper portion of said preheating zone full of pebbles so as to avoid stagnant gas spaces with concomitant deposition of carbon therein; passing the entire preheated feed upwardly through said combustion zone and there burning such a portion of same by admixture with a preheated oxygen-containing gas as to heat and crack said feed to ethylene with concomitant heating of the pebbles in the combustion zone; passing the entire resulting gaseous mixture upwardly through said cracking zone

with continued cracking of ethane in the lower portion and with cooling of the cracking effluent and heating of the pebbles in the upper portion thereof; transferring pebbles from the lower portion of said preheating zone to the upper portion of said cracking zone; and recovering an ethylene-rich stream from the upper portion of said cracking zone.

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