

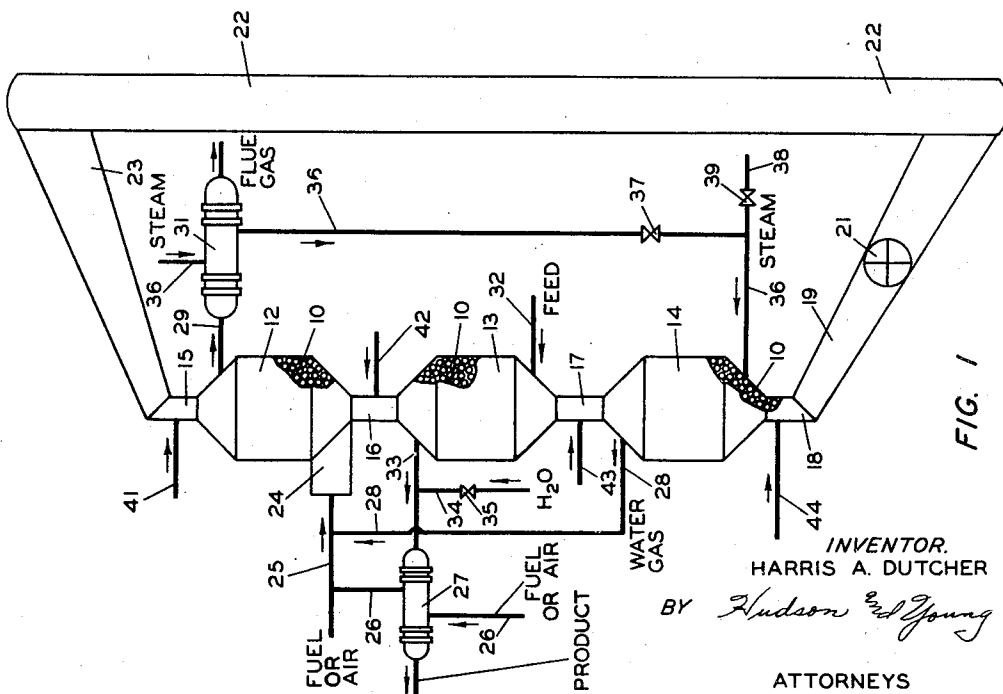
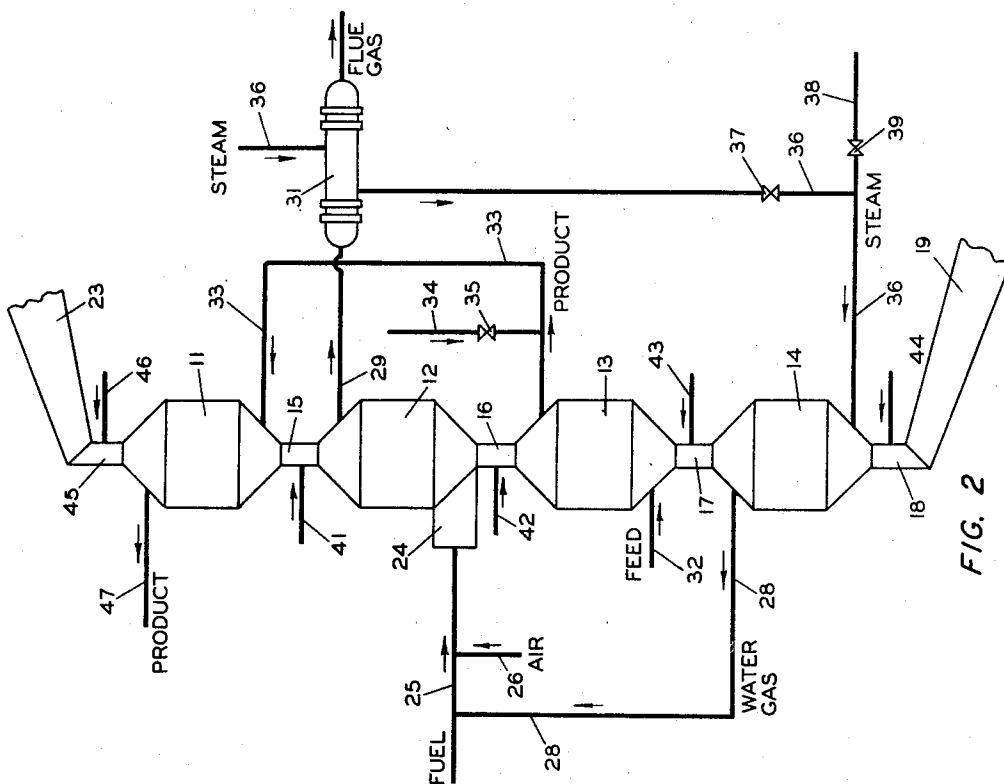
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HYDROCARBON CONVERSION IN PEBBLE HEATERS

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HYDROCARBON CONVERSION IN PEBBLE HEATERS

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This invention pertains to an improved process for conversion of hydrocarbons.

In hydrocarbon conversion processes involving cracking, dehydrogenation, reforming, etc., more or less carbonaceous matter, such as tar or coke, is deposited in the conversion zone. When operating with a stationary catalyst bed, it is necessary to periodically burn off the carbon, thereby reducing conversion time and the rate of production. In order to overcome this disadvantage and obviate periodic on-stream operation, a process has been devised wherein the conversion reaction is carried on in a zone thru which a moving mass of hot heat-transfer material flows, supplying sufficient heat to meet conversion requirements. In some cases the heat-transfer particles are catalytic to the conversion reaction and in others they are relatively inert. In other cases a mixture of catalytic and non-catalytic particulate refractory materials is utilized in a mixed stream.

During operation according to the process just described more or less carbon is formed on the particulate material circulating thru the conversion zone. This particulate material, which may be in the form of small "pebbles," becomes cooled in the conversion zone and must be reheated before returning it to the conversion zone. During the reheating of the pebbles with hot combustion gas containing a regulated amount of oxygen, carbonaceous deposit on the pebbles is removed by combustion. But during this reheating and carbon-removing step, it is difficult to control the temperature thruout the pebble mass, resulting in uneven and excessive temperatures which sometimes cause pebble breakage, fusion, channeling, etc. This is because of uneven carbon distribution and uneven heating generated by combustion thereof. Excessive and uneven heating of pebbles is detrimental to pebbles in many instances, especially when catalytic materials are incorporated therein, and results in inefficient temperature control of the conversion process, itself.

In normal pebble heater operation at conversion temperatures of the order of about 1200° to 3000° F., the pebbles leaving the conversion zone and entering the elevator are too hot to be handled with ordinary high carbon steel elevator or transfer equipment and require special, rather expensive alloy equipment.

It is an important object of the present invention to provide a process for the conversion of hydrocarbons, using pebble heater technique, which permits the removal of carbonaceous de-

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posit from the pebbles with improved control of temperatures and more uniform heating of pebbles in the system.

Another object of the invention is to provide a process for the conversion of hydrocarbons at elevated temperatures, using pebble heater technique, which permits the use of ordinary carbon steel elevator equipment in place of the conventional expensive high temperature alloys.

A further object of this invention is to provide a continuous, efficient process for the conversion of hydrocarbons in which normal carbonaceous deposit from the conversion reaction is utilized as at least a portion of the fuel consumed in producing the heat requirements of the process.

It is also an object of this invention to provide a process for the conversion of hydrocarbons which utilizes sensible heat of effluents from the conversion zone as a portion of the heat requirements of the process.

Other objects, such as the conservation of pebbles, will become apparent from a consideration of the accompanying disclosure.

According to this invention a fluent mass of hot, small, refractory elements, called pebbles, are continuously flowed by gravity thru a series of vertically extending zones including a pebble heating zone, a conversion zone, and a pebble cooling zone; and the pebbles are simultaneously contacted in each zone by a gas having the desired function. These pebbles are preferably spherical and relatively uniform in size but may be rod-shaped or irregular in shape and size. Spheres of about $\frac{1}{8}$ " to 1" in diameter may be utilized but spheres of from about $\frac{1}{4}$ " to $\frac{1}{2}$ " in diameter are most practical. These pebbles must be able to withstand temperatures up to about 3500° F. in some cases, so must be sufficiently refractory at the anticipated highest temperature in the pebble heating chamber in a given conversion process. Pure alumina pebbles which have been heated to about 3500° F. for a substantial period make excellent pebbles. These may be utilized as is, or after impregnation with more active catalyst material. Pebbles comprising beryllia, "Carborundum," mullite, periclase, and zirconia make excellent pebbles in some processes when properly fired. Alumina in pure form when stabilized with a small amount (less than 5%) of an alkali or alkaline earth metal oxide and impregnated with a metal oxide from groups V or VI of the periodic table makes an excellent catalytic pebble capable of withstanding moderately high temperatures, such as 2500° F., suit-

able for dehydrogenation, cracking, and reforming of hydrocarbons.

Pebbles descending thru the pebble heating chamber are contacted by a stream of hot combustion gas, preferably countercurrently, at a temperature and flow rate regulated to insure heating of the pebbles to a temperature substantially above a predetermined conversion temperature in the range of about 1500° to 3000° F. Pebble temperatures at least 100° F. above conversion temperature are desirable and they may advantageously be several hundred degrees above. Since the amount of heat delivered in the conversion zone is dependent upon the difference between pebble inlet temperature and pebble outlet temperature and the quantity of pebbles passed thru this zone, the temperature of conversion can be regulated by controlling these factors. By utilizing high pebble inlet temperatures to the conversion chamber and relatively rapid pebble flow, extremely large heat requirements can be met.

Hot pebbles flowing thru the conversion chamber are continuously contacted with a gaseous stream of a selected hydrocarbon feed, preferably countercurrently, at a flow rate designed to produce the desired amount of conversion. It is desirable to preheat the feed to a temperature substantially below conversion temperature but sufficiently high that there is not too great a gradient in pebble temperature in the conversion chamber. By correlating the pebble inlet temperature, rate of pebble flow, feed preheat temperature, and feed flow rate, desirable conversion temperatures up to about 3200° F. are feasible.

In hydrocarbon conversion reactions involving cracking, dehydrogenation, reforming, etc., carbonaceous material is deposited in the reaction zone and when operating in pebble heater apparatus this is largely deposited on the pebbles. According to the invention, the pebble stream, carrying a substantial amount of carbon, descends thru a third chamber directly below the conversion chamber and is there continuously contacted with a stream of steam passing upwardly thru the pebble stream. When operating under conditions which result in high pebble exit temperatures from the conversion chamber, such as about 1300° F. to 2600° F., it is feasible to react the steam with the carbon on the pebbles to produce water gas. This step in the process not only converts the carbon to utilizable fuel for heating in the pebble heating zone, without overheating the pebbles, but also reduces the pebble exit temperature from this chamber so that pebbles can be transferred and elevated in ordinary carbon steel equipment. The lower part of this pebble cooling chamber serves to raise the temperature of the steam to such a degree that the water gas reaction is initiated in the upper region of the chamber. By proper correlation of the temperature and quantity of steam admitted, the inlet pebble temperature, and pebble flow rate, the pebble stream can be reduced to a temperature at which the necessity for expensive high-temperature alloys in elevator equipment is obviated. This temperature should be in the range of about 500° to 900° F. The amount of steam admitted may well be in excess of that required to remove the carbon from the pebbles since excess steam merely serves as a tempering fluid in both the pebble cooling zone and the pebble heating zone. In cases where it is desirable to pass less steam into the combustion chamber than is present in

effluent may be passed thru a waste heat boiler or condenser to remove a portion of the steam therein. In cases where it is not desirable to utilize the effluents containing water gas in the combustion zone of the pebble heater, this effluent gas may be disposed of in any desirable manner. Such may be the case when only a slight deposition of carbon is taking place in the conversion zone.

In operating at extremely high conversion temperatures, it is often desirable to pass the pebble stream thru a preheating chamber before allowing it to pass into the heater proper and there contact it with the hot effluents from the conversion zone. This step utilizes a considerable portion of the sensible heat of the product gases and desirably cools those gases before they pass to separation means. When selectively cracking or dehydrogenating it adds considerably to yield to quickly quench the effluents from the conversion zone. This may be accomplished by injection of cooling fluids into the effluent line to reduce the temperature to a point at which further reaction is substantially prevented. Quenching to about 800° or 900° F. will usually suffice and the quenched stream still has considerable utility in preheating the pebble stream which may enter this chamber at a temperature as low as about 450° F.

For a more complete understanding of the invention, reference may be had to the accompanying drawing of which Fig. 1 is a diagrammatic showing of a desirable arrangement of equipment for performing the process of the invention. Fig. 2 is a diagrammatic showing of apparatus arranged for performing that embodiment of the invention involving preheating of the pebble stream.

Referring to Figure 1, a fluent mass of pebbles 10, substantially filling heat-insulated chambers 12, 13, and 14, and necks 15, 16, 17, and 18 descends by gravity thru the various chambers of the apparatus and passes thru star valve 21 (or other feeder device) in chute 19 to elevator 22. Elevator 22 transfers the pebbles at a predetermined rate to chute 23 from which they again enter inlet neck 15 and flow thru the system. By regulation of the rate of operation of feeder valve 21 a contiguous column of pebbles is maintained thruout the apparatus below chute 23 so that there are no unnecessary voids in the chambers and necks connecting them. Regulation of the flow of pebbles may also be attained by utilizing a variable speed motor on the elevator, thereby controlling the rate of return of pebbles to the pebble inlet chute.

As pebbles flow thru chamber 12, they are heated to a temperature at least 100° F. above a predetermined conversion temperature by contact with a stream of hot combustion gas from furnace or burner 24. Fuel and air are fed into furnace 24 thru line 25. It is advantageous when operating at high conversion temperatures to preheat the fuel or air and this may be accomplished economically in heat-exchanger 27. Water gas from line 28 is desirably added to the fuel supply in line 25 to furnish at least a portion of the heat requirements in chamber 12. Flue gas passes out thru line 29 and heat-exchanger 31.

Hot pebbles flowing thru conversion chamber 13 are contacted with the gaseous hydrocarbon feed admitted to the bottom of the chamber in a preheated condition via line 32. As the feed passes up thru the descending pebble stream, it

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substantial conversion takes place before leaving chamber 13 via line 33 and heat-exchanger 27 which serves to preheat either air or fuel for combustion purposes. Line 34 controlled by valve 35 introduces quenching fluid to line 33. The pebble stream emerging from chamber 13 passes thru neck 17 into pebble cooling chamber 14 and is contacted by a stream of steam fed in thru line 36 controlled by valve 37 and passing thru heat-exchanger 31. Auxiliary line 38 controlled by valve 39 is utilized to supplement and temper the steam admitted thru line 36. The temperature of steam passed thru line 36 can be increased to any degree required in chamber 14 by heat-exchange with flue gas in exchanger 31. Steam admitted to chamber 14 contacts the hot carbon coated pebbles descending thru the chamber and effects the water gas reaction, producing CO and H₂ which passes via line 28 to fuel line 25, supplying burner or furnace 24.

Operation at pressures varying only slightly from atmospheric such as 0.5 to 5 p. s. i. g. are preferred, but other pressures either above or below atmospheric may be utilized with varying efficiency. Maintenance of substantially equal pressures in the various pebble chambers results in less gas flow between chambers than otherwise. In some types of conversion it may be desirable to operate with a non-deleterious blocking gas, such as steam, in necks 15, 16, 17, and 18, supplied via lines 41, 42, 43, and 44, respectively. The same or different gases may be used in these necks.

The arrangement of apparatus shown in Fig. 2 is similar to that of Fig. 1, but an additional pebble chamber is utilized above pebble heater 12, designated as pebble preheating chamber 11. Pebbles enter chamber 11 from neck 45 and chute 23 (leading from the elevator not shown) and are contacted therein with hot effluents, either quenched or unquenched, from conversion chamber 10, passing in via line 33 and leaving via line 47. Line 46 admits steam or other blocking gas to neck 45. The embodiment of the invention illustrated in Fig. 2 makes it possible to attain extremely high conversion temperatures with sharp heating in the conversion zone without "pushing" the pebble heater proper and with higher heating efficiency.

By way of illustration a feed consisting of 5% methane, 80% ethane, and 15% propane by volume is cracked in a two-chamber pebble heater at about 1600° F. with a reaction time of 0.2 second. The effluent from this first stage has the following composition in volume per cent: 29.8 H₂, 15.1 CH₄, 36.0 C₂H₄, 13.5 C₂H₆, 1.2 C₃H₆, 2.0 C₃H₈, 2.4 C₄'s and heavier.

The effluent resulting from cracking at 1600° F. is passed thru the conversion chamber of a three-chamber pebble heater apparatus, according to the invention, operating at a conversion temperature of about 2500° F. and a reaction time of 0.5 second, using 3/8" alumina spheres as pebbles. During this conversion, the pebble stream enters the pebble heating chamber at about 450° F., is contacted by a stream of combustion gas entering the lower portion of the chamber at about 3200° F. and leaving at about 800° F., and is brought up to a temperature of about 2800° F. During the descent thru the conversion zone, this 2800° F. stream of pebbles drops in temperature to about 1800° F. as a result of heating and converting the feed stream which enters the lower portion of the chamber at about 1600° F. While descending thru the pebble cooling chamber, the

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pebble stream, carrying carbon to the extent of about 5% of the feed by weight, is contacted with a stream of steam entering the lower portion of the chamber at about 240° F. About 5 pounds of steam are fed into the pebble cooling chamber for each pound of carbon entering this chamber with the pebble stream. The pebbles emerge from this chamber at about 600° F. and are substantially free of carbonaceous material. The effluent, containing water gas and steam and at a temperature of about 1200° F., is passed to the combustion chamber as fuel. Pebbles at about 600° F. are transferred in ordinary carbon steel elevator equipment to the inlet to the pebble heating chamber.

The product from the first cracking operation is converted, according to the invention, into the following products by volume per cent: 43.6 H₂, 16.5 CH₄, 20.0 C₂H₄, 11.6 C₂H₆, 2.5 C₃H₆, and 5.8 C₄'s and heavier (including coke).

During the operation, removal of carbon from pebbles is substantially complete and little difficulty in obtaining rather uniform temperatures is experienced. This is in contrast to conventional removal of carbon from catalyst or pebbles in the heating chamber by oxidation, with concomitant localized overheating of the heat-transfer material.

Various modifications of the invention will become apparent to those skilled in the art. The illustrative details disclosed are not to be construed as imposing unnecessary limitations on the invention.

I claim:

1. A continuous process for conversion of hydrocarbons at elevated temperatures which comprises continuously flowing a fluent contiguous mass of hot refractory pebbles thru a series of substantially vertically extending zones comprising a pebble heating zone, a pebble cooling zone positioned below said pebble heating zone, and a conversion zone positioned intermediate said zones and communicating therewith thru relatively narrow zones, each of said zones being substantially filled with said pebbles and permitting relatively unrestricted flow of pebbles there-thru; continuously contacting that portion of said contiguous mass of pebbles flowing thru said pebble heating zone with a stream of hot combustion gas at a temperature and flow rate regulated to insure heating of said pebbles to a temperature substantially above a predetermined conversion temperature; continuously contacting that portion of said contiguous mass of pebbles flowing thru said conversion zone with a stream of hydrocarbon gas at a flow rate regulated to insure heating of said hydrocarbon gas to said conversion temperature and substantial conversion thereof to desired products whereby carbonaceous material is deposited on said pebbles; continuously contacting that portion of said contiguous mass of pebbles flowing thru said pebble cooling zone with a stream of superheated steam at a temperature and flow rate regulated to insure substantial removal of carbonaceous deposit from said pebbles by the water gas reaction and substantial cooling thereof with concomitant production of water gas; continuously burning said water gas with other fuel to produce said hot combustion gas; continuously removing pebbles from said pebble cooling zone; continuously introducing pebbles to said pebble heating zone; and continuously recovering effluents from said conversion zone.

2. The process of claim 1 in which pebble flow

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and gas flow in pebble heating zone, conversion zone, and pebble cooling zone are countercurrent.

3. The process of claim 1 in which conversion temperature is in the range of about 1500° to 3000° F. and pebble exit temperature from the conversion zone is in the range of about 1300°-2600° F.

4. The process of claim 1 in which the pebbles are catalytic with respect to the conversion reaction.

5. A continuous process for conversion of hydrocarbons to more desirable hydrocarbons at elevated temperatures which comprises continuously flowing a fluent contiguous mass of hot refractory pebbles thru a series of substantially vertically extending zones comprising a pebble heating zone, a pebble cooling zone positioned below said pebble heating zone, and a conversion zone positioned intermediate said zones and communicating therewith thru relatively narrow zones, each of said zones being substantially filled with said pebbles and permitting relatively unrestricted flow of pebbles therethru; continuously contacting that portion of said contiguous mass of pebbles flowing thru said pebble heating zone with a stream of hot combustion gas at a temperature and flow rate regulated to insure heating of said pebbles to a temperature substantially above a predetermined conversion temperature in the range of 1500 to 3000° F.; continuously contacting that portion of said contiguous mass of pebbles flowing thru said conversion zone with a stream of hydrocarbon gas at a flow rate regulated to insure heating of said hydrocarbon gas to said conversion temperature and substantial conversion thereof to desired hydrocarbon products whereby carbonaceous material is deposited on said pebbles; continuously contacting that portion of said contiguous mass of pebbles flowing thru said pebble cooling zone at an initial pebble temperature in the range of 1300 to 2600° F. with a stream of superheated steam at a temperature and flow rate regulated to insure substantially complete removal of carbonaceous deposit from said pebbles by the water gas reaction and cooling thereof to a temperature between about 500° and about 900° F.; continuously removing pebbles from said pebble cooling zone; continuously introducing pebbles to said pebble heating zone; and continuously recovering converted hydrocarbons from said conversion zone.

6. The process of claim 5 in which pebble flow and gas flow in pebble heating zone, conversion zone, and pebble cooling zone are countercurrent.

7. The process of claim 5 in which the pebbles are catalytic with respect to the conversion reaction.

8. A continuous process for conversion of hydrocarbons at elevated temperatures which comprises continuously flowing a contiguous fluent mass of hot refractory pebbles by gravity thru a series of substantially vertically extending zones comprising from highest to lowest a pebble preheating zone, a pebble heating zone, a conversion zone, a pebble cooling zone, and several relatively narrow connecting zones for permitting relatively free flow of pebbles between said zones, all of said zones being substantially filled with said mass of pebbles; continuously contacting that portion of said mass of pebbles in said pebble preheating zone with a stream of gaseous effluents from said conversion zone to substantially preheat said pebbles; continuously contacting that portion of said mass of pebbles in said pebble heating zone with a stream of hot combustion gas whereby said pebbles are heated to a temperature sub-

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stantially above a predetermined conversion temperature; continuously contacting that portion of said mass of pebbles in said conversion zone with a stream of hydrocarbon gas to be converted at a flow rate regulated to insure maintenance of said predetermined conversion temperature and substantial conversion of hydrocarbon to desired products with concomitant deposition of carbonaceous material on said pebbles; continuously contacting that portion of said mass of pebbles in said pebble cooling zone with a stream of superheated steam at a temperature and flow rate regulated to insure substantial removal of said carbonaceous material from said pebbles by the water gas reaction and substantial cooling thereof with concomitant production of water gas; continuously burning said water gas to produce at least a portion of said combustion gas used in the pebble heating zone; continuously removing pebbles from said pebble cooling zone; continuously introducing pebbles to said pebble preheating zone; and continuously recovering the effluents from the conversion zone.

9. The process of claim 8 in which conversion temperature is in the range of about 1500° to 3000° F. and pebble exit temperature from the conversion zone is in the range of about 1300°-2600° F.

10. A continuous process for conversion of hydrocarbons to more desirable hydrocarbons at elevated temperatures which comprises continuously flowing a contiguous fluent mass of hot refractory pebbles by gravity thru a series of substantially vertically extending zones comprising from highest to lowest a pebble preheating zone, a pebble heating zone, a conversion zone, a pebble cooling zone, and several relatively narrow connecting zones for permitting relatively free flow of pebbles between said zones, all of said zones being substantially filled with said mass of pebbles; continuously contacting that portion of said mass of pebbles in said pebble preheating zone with a stream of gaseous effluents from said conversion zone to substantially preheat said pebbles; continuously contacting that portion of said mass of pebbles in said pebble heating zone with a stream of hot combustion gas whereby said pebbles are heated to a temperature substantially above a predetermined conversion temperature in the range of 1500 to 3000° F.; continuously contacting that portion of said mass of pebbles in said conversion zone with a stream of hydrocarbon gas to be converted at a flow rate regulated to insure maintenance of said predetermined conversion temperature and substantial conversion of hydrocarbon to desired hydrocarbon products with concomitant deposition of carbonaceous material on said pebbles; continuously contacting that portion of said mass of pebbles in said pebble cooling zone at an initial pebble temperature in the range of 1300 to 2600° F. with a stream of superheated steam at a temperature and flow rate regulated to insure substantially complete removal of said carbonaceous material from said pebbles by the water gas reaction and cooling thereof to a temperature in the range of 500 to 900° F.; continuously removing pebbles from said pebble cooling zone; continuously introducing pebbles to said pebble preheating zone; and continuously recovering the converted hydrocarbons from the conversion zone.

11. In a process of converting hydrocarbons at elevated temperatures to desirable products wherein a fluent contiguous mass of refractory pebbles is circulated by gravity thru a series of

zones comprising a pebble heating zone and a conversion zone communicating thru a relatively narrow elongated zone and permitting relatively free flow of pebbles therethru, said zones being substantially filled with said mass of pebbles; wherein that portion of said mass of pebbles flowing thru said pebble heating zone is continuously contacted with a stream of hot combustion gas to heat said pebbles to a temperature substantially above a predetermined conversion temperature and that portion of said mass of pebbles flowing thru said conversion zone is continuously contacted with a stream of hydrocarbons to heat and convert the same to desirable products; and wherein carbonaceous matter is deposited on said pebbles in said conversion zone; the improvement which comprises flowing said mass of pebbles from said conversion zone thru a pebble cooling zone and there continuously contacting said mass of pebbles with a stream of steam at a temperature and flow rate regulated to insure substantial removal of said carbonaceous matter from said pebbles by the water gas reaction and substantial cooling of said pebbles and continuously burning the water gas produced to form at least a portion of said hot combustion gas.

12. In a process of converting hydrocarbons to more desirable hydrocarbons at elevated temperatures to desirable products wherein a fluent contiguous mass of refractory pebbles is circulated by gravity thru a series of zones comprising a pebble heating zone and a conversion zone communicating thru a relatively narrow elongated zone and permitting relatively free flow of pebbles therethru, said zones being substantially filled with said mass of pebbles; wherein that portion of said mass of pebbles flowing thru said

pebble heating zone is continuously contacted with a stream of hot combustion gas to heat said pebbles to a temperature substantially above a predetermined conversion temperature in the range of 1500 to 3000° F. and that portion of said mass of pebbles flowing thru said conversion zone is continuously contacted with a stream of hydrocarbons to heat and convert the same to desirable hydrocarbon products; and wherein carbonaceous matter is deposited on said pebbles in said conversion zone; the improvement which comprises flowing said mass of pebbles from said conversion zone thru a pebble cooling zone separated from said conversion zone and there continuously contacting said mass of pebbles at an initial pebble temperature in the range of 1300 to 2600° F. with a stream of steam at a temperature and flow rate regulated to insure substantially complete removal of said carbonaceous matter from said pebbles by the water gas reaction and substantially cooling of said pebbles to a temperature in the range of 500 to 900° F.

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