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CONVERSION OF HYDROCARBONS

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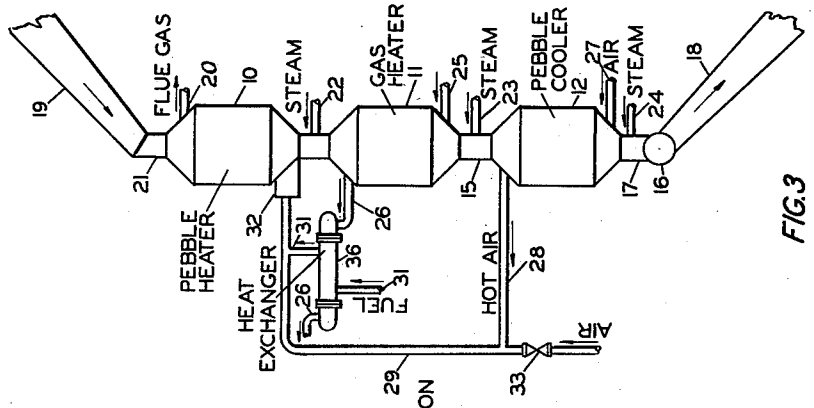


FIG.3

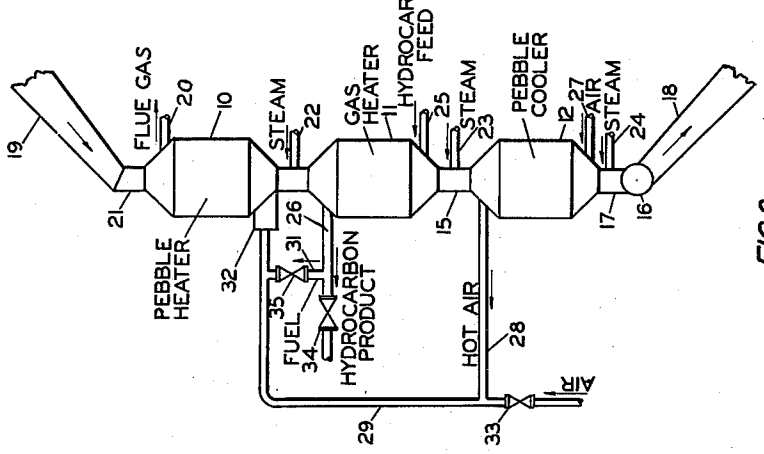


FIG.2

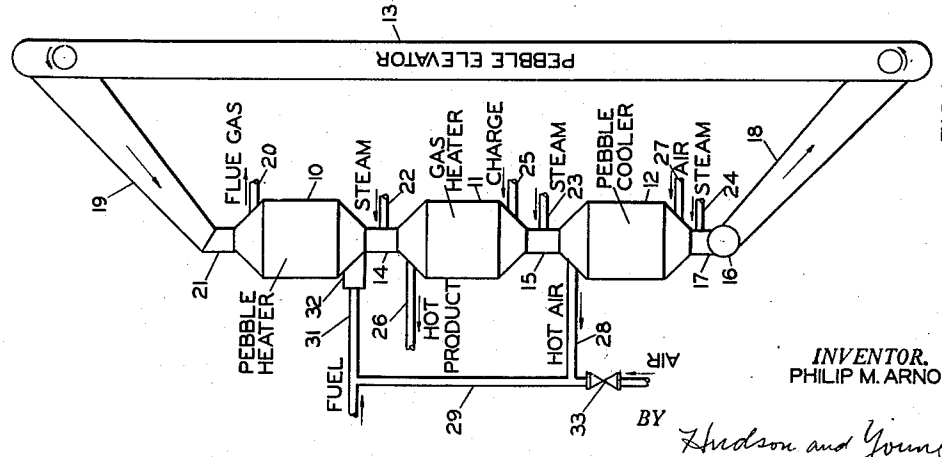


FIG.1

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CONVERSION OF HYDROCARBONS

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4 Claims. (Cl. 196—55)

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This invention relates to methods and apparatus for heating gases to high temperatures.

A particular embodiment of the invention relates to methods and apparatus for heating hydrocarbon gases to high temperatures for conversion thereof to other carbon and hydrogen-containing gases.

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 thru 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 thru the system.

In processes which function most advantageously at extremely high temperatures, for example in the thermal cracking of light hydrocarbons to produce lighter fractions such as acetylene, the pebbles leaving the cracking chamber are still at a very high temperature and can be handled in elevator equipment only if high temperature alloy materials are used. Furthermore, in conventional apparatus it is difficult, if not impractical, to attain the high temperatures that are so advantageous in the cracking of the lighter hydrocarbons to produce acetylene wherein temperatures of 3000° F. to 3500° F. are especially desirable.

It is an object of the present invention to provide arrangements of apparatus and processes which facilitate the attainment of extremely high temperatures in a pebble heater.

Another object of this invention is to provide improvements in processes for heating hydrocarbon gases to high temperatures for conversion processes.

A further object is to obtain a lower pebble temperature in the elevator apparatus so that expensive alloy equipment is not required, without lowering the heating efficiency of the pebble heater type apparatus.

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

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In one embodiment of the invention the hot pebbles flowing from the hydrocarbon conversion chamber are passed through a third chamber in intimate contact with a stream of air passing therethru. This step cools the pebbles to a temperature below that above which special high temperature alloys are required in the elevator. As a further refinement of this feature of the invention, the hot air emanating from the third chamber, which is both an air-heating chamber and a pebble-cooling chamber, is passed to the first or pebble heating chamber where it is utilized to burn fuel for heating the pebbles.

In another embodiment of the invention a portion of the effluent hydrocarbon product from the cracking or conversion chamber is passed to the combustion zone as fuel, thereby utilizing preheated fuel and attaining a higher temperature for the process than is otherwise attained. This feature is also combined with preheating of the air fed to the combustion fuel in order to obtain the extremely high temperatures so effective in the pyrolysis of light hydrocarbons for acetylene production. This modification is preferred when the feed is relatively cheap and the concentration of the product in the effluent is relatively low.

In still another embodiment of the invention the fuel fed to the combustion zone is preheated by indirect heat exchange with the hot effluent product from the conversion chamber. This expedient is double-edged in that hotter pebbles are obtained by preheating the feed and a desirable cooling of the product is obtained. Preheating of the fuel by this method is preferred where the product being manufactured is too expensive to be used as fuel and where there is a high concentration of the desired product in the effluent gases from the conversion chamber.

This invention may also be applied to the heating of gases such as steam, air, nitrogen, etc., where high temperature without contamination of the gases is desired.

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 ⅛" to about 1" in diameter with the preferred size for high temperature processes about ¼". 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.

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 apparatus arranged so as to preheat combustion air and cool pebbles before they are transferred into the elevator.

Figure 2 is a diagrammatic showing of a suitable arrangement of apparatus for preheating the air for fuel combustion and simultaneously feeding preheated fuel, a portion of the product hydrocarbons, to the combustion zone.

Figure 3 shows diagrammatically a preferred arrangement of apparatus for preheating the fuel by indirect heat exchange with the hot effluent product from the conversion reaction.

In Figure 1, 10 is an insulated, refractory lined heating chamber for heating flowable pebbles of a ceramic or metallic composition; 11 and 12 are heating chambers of similar construction, the former for heating the gases being processed, the latter for preheating air for aiding the combustion required for heating chamber 10; and 13 is an elevator of the continuous, bucket type for transferring pebbles from chamber 12 to chamber 10 for reheating and recycling thru the system. Chambers 10, 11, and 12 are arranged at successively lower levels and connected by conduits 14 and 15 to accommodate the natural flow of pebbles through the apparatus. A star wheel 16, or similar device, in conduit 17 controls the rate of flow of pebbles through the apparatus and feeds the pebbles into conduit 18 leading into elevator 13. Proper screening devices may be inserted in conduit 18 for removing fines and broken pebbles through a closable opening not shown. Pebbles reaching the top of the elevator are dumped into conduit 19 from which they flow thru conduit or inlet means 21 into heater 10 for reheating and recycling. Conduit 19 is provided with means not shown for introducing fresh pebbles to the system. Lines 22, 23, and 24 are steam lines 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 sub-atmospheric, atmospheric, or superatmospheric as desired.

The hydrocarbon or other gas feed is introduced to heater 11 through line 25 and the product is removed through line 26. Lines 27 and 28 admit to and remove air from chamber 12, line 28 being connected to line 29 which feeds air via line 31 to furnace 32 connected with pebble heater 10. Line 31 feeds fuel to furnace 32 connected with heater 10 and line 20 carries combustion gas out of heater 10. Valve 33 in line 29 serves to admit air from any convenient source for tempering purposes or as an independent supply when desired.

In Figure 2 the arrangement is varied so as to permit the utilization of preheated fuel along with preheated air as in Figure 1. Fuel line 31 is connected to product gas line 26 leading from the hydrocarbon conversion chamber 11. Valve 34 in line 26 and valve 35 in line 31 serve to control the proportion of product gas utilized as fuel.

Figure 3 sets forth an arrangement of apparatus which permits the preheating of an independent fuel supply by indirect heat exchange with the hot effluent gas from heating chamber 11. Heat exchanger 36 is inserted in lines 26 and 31 to effect the desired preheating of fuel gas flowing through line 31.

This invention is especially advantageous in the production of acetylene. Light hydrocarbon gases are cracked at a temperature of 1400° to 2000° F. in chamber 11 of Figure 1 under conditions to produce an abundance of ethylene. The ethylene-containing effluent from chamber 11 is fed into a second pebble heater apparatus, such as shown in Figures 2 or 3, which involves preheating both the air and fuel in this second system and attains a temperature of from about 3000° to 3500° F. The use of such high temperatures in cracking light hydrocarbons such as ethylene to produce acetylene made attainable by this invention results in a much greater concentration of acetylene in the product gases and a much more economical production of acetylene. The prior art method of producing acetylene at temperatures up to about 3000° F. entails dilution of the product gases with combustion gases, due to direct contact with burning fuels, thereby adding to the cost of recovering acetylene. The present invention makes it possible to produce more acetylene from a given amount of feed and a much higher concentration of acetylene in the product gas.

In the production of acetylene by thermal cracking or thermal dehydrogenation of ethylene at high temperatures in a pebble heater, the expedient of utilizing a part of the hot effluent product from the conversion zone for fuel in the combustion zone is especially desirable and makes it possible to attain temperatures up to about 3500° F. in the conversion zone. Such high temperature operation requires the use of the best electric furnace refractories in the hottest areas of the combustion and conversion zones. Pebbles of a correspondingly high quality are likewise essential. It is found that the smaller more dense pebbles stand up best under the more severe conditions of temperature. Pebbles of approximately $\frac{5}{8}$" to $\frac{1}{4}$" diameter and relatively high density are more spall resistant and suffer less breakage than larger pebbles; they also have more heating surface for a given volume and hence are more efficient. Pebbles must be sufficiently large and dense to permit high feed flow rates without being suspended or lifted by countercurrent gas flow, the preferred technique.

In operation refractory pebbles fill the three heating chambers 10, 11, and 12, and the connecting conduits, their flow through the system being regulated by operation of star wheel 16 in conduit 17 according to the temperature required in conversion chamber 11. Where heating demands are high, more rapid flow of hotter pebbles is required than where they are low. Pebbles are heated in chamber 10 by combustion gases flowing therethru from furnace 32 which is supplied fuel from any convenient source through line 31 and preheated air from line 29. The rate of combustion and degree of preheating of the air and/or fuel determine the temperature attained in heater 10. Combustion gases withdrawn through line 20 can be utilized in any desirable manner to recover the sensible heat thereof. Heated pebbles are permitted to flow through chamber 11 at a rate and temperature which insures the maintenance of the desired conversion temperature therein. The higher the temperature differential between pebble temperature and conversion temperature, the slower will be the rate of flow and vice versa. At the higher conversion temperatures, e. g., above 3000° F., more rapid pebble flow rates are required, assuming other factors constant.

The gas to be heated or processed is fed into chamber 11 via line 25 and the hot product is discharged through line 26 after being contacted and heated by the hot pebbles flowing through the chamber. In chamber 11 the pebbles give up considerable heat to the feed gas but enter chamber 12 via conduit 15 at a temperature often considerably in excess of 1000° F. and are cooled by air being passed through this zone, via lines 27 and 28, so that their high temperature will not result in damage to the elevator equipment. Cooled pebbles leave zone 12 through conduit 17, their flow being regulated by feeder or star wheel 16, and flow into conduit 18 which allows them to descend to the lower portion of elevator 13. Elevator 13 carries the pebbles to the upper end of conduit 19 where they are dumped and flow therethru into conduit 21 and heater 10.

The flow of air through zone 12 is regulated to provide the desired cooling effect on the pebbles and the extent of preheating of the air advantageous to the degree of heating desired in chamber 10. This preheated air is passed via lines 28, 29 and 31 to furnace 32 for supporting combustion of fuel fed in thru line 31. It may be tempered with air admitted through valve 33 in line 29. The combustion fuel may be preheated as shown in Figure 3 by passing it through an indirect heat exchanger 36, or it may be taken from line 26 as shown in Figure 2, as a portion of the hot effluent from chamber 11, in a case where the gas being processed is a hydrocarbon.

While this invention is particularly advantageous in the production of ethylene and acetylene, it has wide application to thermal cracking and dehydrogenation of the lighter hydrocarbons. It has special utility where rapid heating, careful control of temperature, and high temperatures are demanded. In endothermic reactions requiring rapid transfer of large quantities of heat, the apparatus and method of this invention offer their highest utility. An important advantage of the invention is that there is substantially no dilution or contamination of the product gases with combustion gases as there is in directly heating the feed gases by combustion of fuel. Another advantage is the avoidance of frequent interruptions or shutdowns to burn out deposited carbon in the conversion chamber. In the process of the invention, most of the carbon formation is on the pebbles and is extremely light due to the short contact time between the pebbles and the gases being cracked or dehydrogenated.

I claim:

1. A process for the conversion of hydrocarbons which comprises gravitating a contiguous mass of pebbles through a series of superposed zones connected by relatively narrow pebble passageways, including a pebble heating zone, a conversion zone, and a pebble cooling zone in descending order; contacting that section of said mass of pebbles in said pebble heating zone with hot combustion gas so as to heat the same to a temperature above conversion temperature; contacting the resulting hot pebbles in said conversion zone with a stream of hydrocarbon so as to heat and convert the same to desirable product; contacting that section of pebbles in said pebble cooling zone with a stream of oxygen-containing gas so as to cool said pebbles and heat said gas; recovering heated oxygen-containing gas and a portion of the hydrocarbon conversion effluent and forming a combustible mixture thereof; burning said mixture in said pebble heating zone so as to form the combustion gas for the pebble heating step; and recovering converted hydrocarbon.

2. The process of claim 1 in which the conversion process comprises cracking.

3. The process of claim 1 in which the conversion process comprises cracking light hydrocarbons to acetylene.

4. In an apparatus for heating hydrocarbon gases to high temperatures by contact with a stream of hot pebbles, the combination of a first heating chamber for heating said pebbles by heat of fuel combustion, supply and discharge conduits leading to and from said first heating chamber for continuous flow of fuel thereto and combustion gas therefrom, a second heating chamber for heating the hydrocarbon gases being disposed at a lower level than said first heating chamber, supply and discharge conduits leading to and from said second heating chamber for flow of said gases therethrough, conduit means communicating between the discharge conduit in said second heating chamber and the fuel supply conduit in said first heating chamber for continually passing a part of the effluent hydrocarbon gases from the second heating chamber to the first heating chamber, conduit means in communication with the first and second heating chambers for gravity flow of pebbles therebetween, a third heating chamber for heating air for fuel combustion in the first heating chamber being disposed at a lower level than the second heating chamber, supply and discharge conduits leading to and from said third heating chamber for flow of air therethrough, conduit means for continuously passing heated air from the discharge means of the third heating chamber to the supply means of the first heating chamber for fuel combustion, conduit means in communication with the second and third heating chambers for gravity flow of hot pebbles therebetween, an inlet in the first heating chamber for admitting pebbles, an outlet in the third heating chamber for withdrawing pebbles, and means for transferring pebbles from said outlet to said inlet.

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