Jan. 8, 1952 H. A. DUTCHER 2,582,016

PROCESS FOR THE PRODUCTION OF ACETYLENE

Filed Feb. 14, 1946

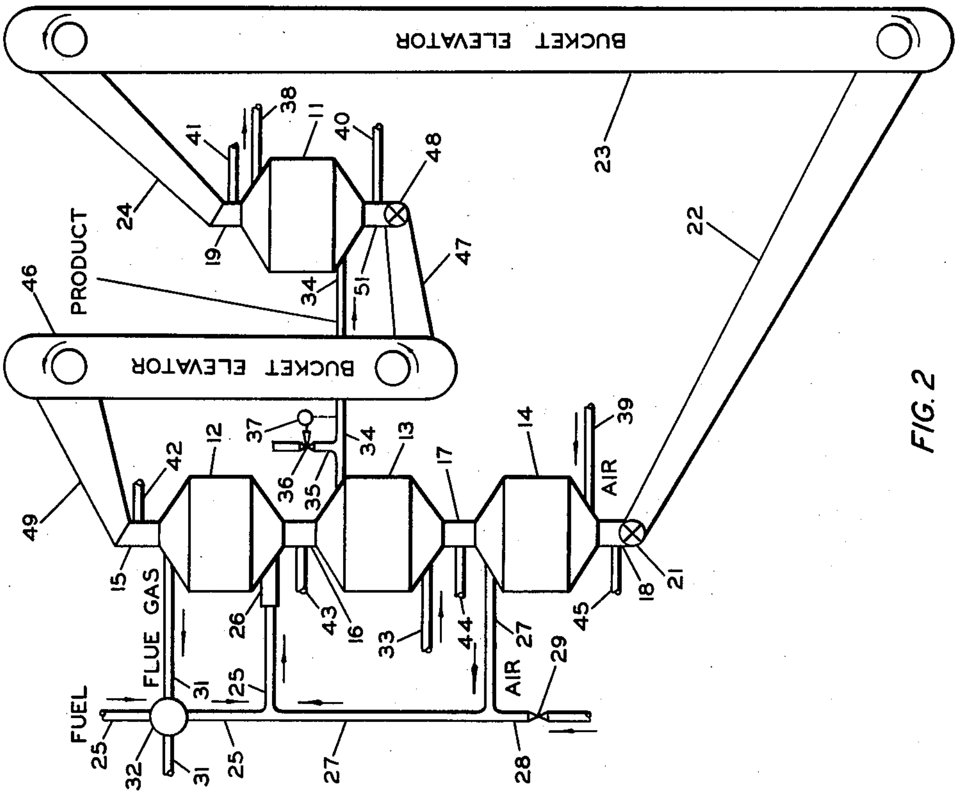

FIG. 2

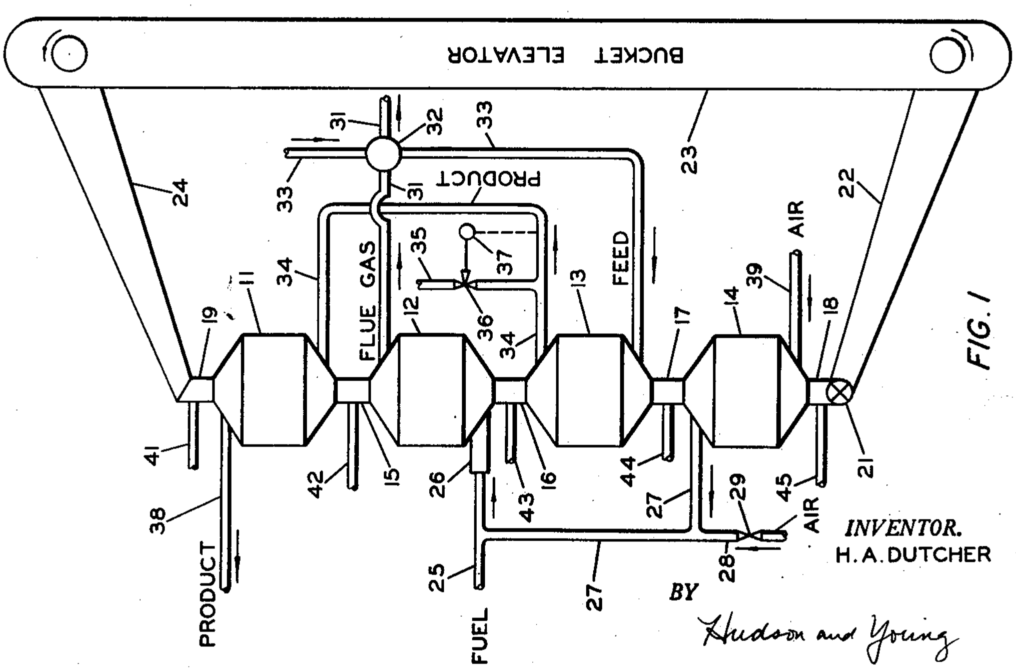

FIG. 1

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Patented Jan. 8, 1952 2,582,016

UNITED STATES PATENT OFFICE

2,582,016

PROCESS FOR THE PRODUCTION OF ACETYLENE

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Application February 14, 1946, Serial No. 647,589

1 Claim. (Cl. 196—55)

This invention relates to methods and apparatus for conducting high temperature reactions.

One particular embodiment of the invention relates to methods and apparatus for high temperature conversion of hydrocarbons to other carbon- and hydrogen-containing compounds.

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. A third chamber is sometimes placed below the conversion chamber to receive and cool the pebbles by contact with a stream of air before being transferred by the elevator to the pebble heating chamber. The air heated by the pebbles in the cooling chamber is passed to the combustion zone of the pebble heater to support fuel combustion and permit attainment of higher temperatures in the pebble heater than would be possible without preheated air.

While this practice of cooling the pebbles in their circulation between the conversion chamber and the elevator avoids the necessity for high temperature alloy equipment in the elevator and provides for the use of preheated air for fuel combustion, it necessitates an extremely high differential between pebble inlet and outlet temperatures in the pebble heater and thereby increases fuel consumption and places a lower limit on maximum temperatures attainable therein than is obtainable by this invention. In conventional procedure, there is also a lack of utilization of the large amount of sensible heat in the effluent hydrocarbons from the conversion zone which may be at a temperature of from about 1400° to more than 3000° F. depending upon the particular process involved.

It is an object of the present invention to permit lower pebble temperature in elevator equipment without proportionately limiting the maximum temperature obtainable in the conversion zone.

It is a further object of the present invention to provide arrangements of apparatus and processes which facilitate the utilization of the sensible heat of processed hydrocarbon gases in pebble-heater-type apparatus and thereby to permit the attainment of higher temperatures in the conversion zone than are conventional in such apparatus and processes.

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

In one embodiment of the invention, a pebble preheating chamber is positioned above the pebble heater in a conventional pebble-heater-type apparatus and the pebbles passing therethru are preheated by contact with hot effluent conversion products from the conversion chamber. This procedure desirably cools the conversion products and raises the temperature of the pebbles, thereby decreasing the differential between the pebble inlet and outlet temperatures in the pebble heating chamber and making it feasible to attain pebble temperatures in the neighborhood of 3700° F.

In another embodiment of the invention the effluent products from the conversion chamber are quenched to such a temperature as will prevent or decrease further reactions therein before being passed thru the pebble preheating chamber. It is found that in some cases, the quenching of the processed material in the pebble preheater is entirely too slow to adequately prevent continued reactions within and between the various constituents. In such cases, quenching of the reaction products immediately after they leave the conversion chamber by the direct injection of water or other cooling fluid, prevents further reaction by lowering the temperature without any substantial loss in sensible heat available for use in the pebble preheater.

The invention has particular application in thermal cracking and dehydrogenation processes which can be most advantageously performed at temperatures of about 2000°–3500° F., but it also has application to processes operating in the range of 1100°–2000° F. A specific application of the invention is in the cracking of light hydrocarbons to produce ethylene at about 2000° F. in pebble heater apparatus and then passing the hot product to a pebble heater system including a pebble preheater and a pebble cooler, thereby cracking the ethylene to acetylene at temperatures in the range of about 3000°–3500° F.

Another application of the invention is in the cracking of propane at temperatures of 1800°–

3000° F. to produce a fuel gas of about 700 B. t. u. for supplementing city gas system supplies.

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 about 1/8" to about 1" in diameter with the preferred size for high temperature processes about 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. They may be of ceramic, metal, or other refractory materials. It is important that the pebbles be quite dense in order to permit high gas flow rates without entrainment of pebbles in the effluent gases from any of the chambers. Pebbles composed of alumina, beryllia, "carborundum," mullite, periclase, and zirconia when properly fired serve very well at high temperatures, some of them withstanding temperatures up to at least 4000° F. It is desirable when operating in the conversion zone at the higher temperatures to use the best high temperature refractories, at least in the hottest areas of the pebble heating chamber and in the combustion furnace.

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 to preheat pebbles with quenched effluents from the conversion zone along with preheating the feed and the air for the combustion zone.

Figure 2 shows diagrammatically an arrangement of apparatus showing a modification in which the pebble preheater is positioned close to the conversion chamber permitting a short flow line therebetween and in which the air and fuel are preheated and the products are quenched before entering the preheater.

While the processes and apparatus of the invention are particularly applicable to the conversion of hydrocarbons, they have a wide application to endothermic reactions generally. Such processes as the manufacture of carbon disulfide from gaseous hydrocarbons and sulfur-containing gases, and the manufacture of HCN from ammonia and methane may advantageously be carried out according to the present invention. The limitation of the ensuing remarks to the production of hydrocarbons is not to be construed as a limitation of the invention to such processes.

Referring more particularly to Figures 1, 11, 12, 13 and 14 are four refractory lined chambers disposed one above the other, each communicating with the one below it through conduits 15, 16 and 17. Conduits 18 and 19 are outlet and inlet means for flow of pebbles out of chamber 14 and into chamber 11, respectively. Star wheel 21, or other flow-control device, conduit 22, bucket elevator 23, and conduit 24 complete the pebble flow circuit. In operation pebbles are admitted to chamber 11 and flow by gravity thru the other chambers in succession, each of which, along with the connecting conduits, is substantially filled with these heat-carrying pebbles of a refractory nature. The pebble flow is controlled by star wheel 21 which feeds pebbles into conduit 22 and thence into the elevator 23 which returns them to pebble preheater 11 via conduits 24 and 19 to complete the cycle. This technique of operation inherently results in maintaining a compact, contiguous stream of pebbles in the various treating chambers, including the connecting throats, extending from the inlet of the uppermost chamber 11 to the pebble flow-control device 21 below the outlet of the lowermost chamber 14. A screening device in 22, not shown, separates fines and broken pebbles for removal thru a trap door not shown. A door in conduit 24, not shown, may be utilized to add pebbles to the system for replacement or initial operation.

In operation any desirable fuel is fed thru line 25 into burner or furnace 26 mixed with air from line 27 and is burned to produce the desired heating of pebbles in chamber 12. Additional air requirements may be supplied thru line 28, controlled by valve 29. The hot combustion gases from burner 26 pass thru chamber 12 countercurrently to the flow of pebbles therethru and pass out of the chamber to indirect heat exchanger 32 via line 31. The hydrocarbon feed to be converted is passed thru heat exchanger 32 via line 33 into conversion chamber 13 where it is heated by hot pebbles flowing downwardly thru the chamber. Effluent gases from conversion chamber 13 are quenched in line 34 by a relatively cold fluid admitted thru line 35 which is controlled by valve 36. Valve 36 is operated by temperature recorder controller 37 which responds to temperature changes in line 34, automatically regulating the amount of quenching fluid admitted to line 34 to maintain a predetermined temperature therein. The quenched hydrocarbons in line 34 pass thru pebble preheater 11 in intimate contact with a stream of pebbles therein, giving up heat to the pebbles and passing to further treating apparatus via line 38.

In order to simultaneously heat air for fuel combustion in burner 26 and cool pebbles before passing them into elevator 23, air is admitted to chamber 14 via line 39 and is taken off via line 27 which feeds hot air to burner 26. Lines 41, 42, 43 and 45 supply steam to the areas between chambers in order to minimize escape of gases from chamber to chamber.

Where it is preferred to have a short flow line for hydrocarbon effluents from the conversion chamber, the arrangement shown in Figure 2 is advantageous. Line 34 can be made exceedingly short to bring the hot hydrocarbons into contact with cooler pebbles in chamber 11 in the shortest possible time to provide for an earlier quench. However, the gaseous products may be quenched in line 34, just as in the modification illustrated in Figure 1, by injecting cool fluid into the line thru line 35. This arrangement necessitates additional elevator equipment such as pebble outlet 51, star valve 48, conduits 47 and 49, and bucket elevator 46 for conveying the pebbles from the outlet of pebble preheater 11 to the inlet of pebble heater 12.

In the modifications shown in both Figure 1 or Figure 2, the hot effluent combustion gas from the pebble heater may be used to preheat either the fuel or the hydrocarbon feed. In cases where a hot hydrocarbon feed is available preheating of the fuel is feasible. Such is the case where light hydrocarbons are cracked to produce ethylene and the hot ethylene is further cracked at higher temperatures to produce acetylene. The hot ethylene can be fed into chamber 13 without any further preheating allowing opportunity to preheat the fuel by indirect heat exchange with effluent combustion gas.

The apparatus and processes of the invention permit much flexibility as to operating conditions. The rate of pebble flow thru the system can readily be adjusted and correlated with the differential between conversion temperature and pebble inlet temperature to the conversion chamber so as to maintain the desired rate of heating. The heat requirements in the conversion zone depend upon the sensible heat required and the heat of reaction. Preheating the feed to varying degrees will of course decrease the sensible heat required in the conversion zone. The conditions of operation will vary according to the specific process or product desired. It is found that the temperature in the reaction zone may be varied from about 1100° to 3500° F. by controlling the rate of flow of pebbles, the amount of preheating of fuel, feed, and combustion air, and the amount of fuel consumed in the burner attached to the pebble heater. Pebbles will vary in temperature, as they leave the pebble heater, from about 1500° to well above 3500° F. and will be cooled to a temperature within the range of about 800° to 2000° F. as they leave the conversion zone. Pebble outlet temperature in the air heater will vary from about 500° to 900° F. depending upon the entering temperature and the amount of heating of air taking place. It is found that air may be heated to temperatures of about 500° to 1000° and that adequate supplies of air may be preheated within this range.

Effluents from the conversion zone will not always require quenching and may be cycled thru the pebble preheater to be quenched by contact with cooler pebbles therein. In most cases, however, it is desirable, and highly essential in others, that the hot hydrocarbons leaving the conversion zone be immediately quenched to within the range of about 900° to 1400° F. Since pebbles admitted to the preheater are at a temperature of about 450° to 850° F. they can be preheated with the effluent hydrocarbons to a temperature within the range of about 700° to 1200° F.

Combustion gases passing thru the indirect heat exchanger are in the range of about 900° to 1500° F., depending upon the temperature maintained in the pebble heater (combustion zone) and the rate of flow of pebbles therethru. With this available source of heat, either feed or fuel gases may be heated to temperatures within the range of about 500° to 1050° F.

Various pressures from subatmospheric to superatmospheric may be used in the apparatus but only small variations in pressures from zone to zone, e. g., 2 or 3 p. s. i., are practicable. It is preferred to operate at or near atmospheric pressure.

As an illustration of the invention, when about 30 mols per hour of propane are cracked at a temperature of about 2500° F. to produce a domestic fuel gas by passing propane thru a pebble heater arrangement similar to that of Figure 1, in contact with ¼" dense alumina pebbles, the following operating conditions obtain:

Pebble heater

Pebble inlet temperature, °F.	1145
Pebble outlet temperature, °F.	3010
Flue gas outlet temperature, °F.	1515
Pebble circulation, pounds per hour	5120

Conversion chamber

	°F.
Pebble inlet temperature	2995
Pebble outlet temperature	1505
Feed inlet temperature	900
Product outlet temperature	2495
Temperature after water quench	1300

Air heater

	°F.
Pebble inlet temperature	1500
Pebble outlet temperature	695
Air inlet temperature	100
Air outlet temperature	985

Pebble preheater

	°F.
Pebble inlet temperature	645
Pebble outlet temperature	1155
Product+steam inlet temperature	1295
Product+steam outlet temperature	700

From the above data some of the advantages of the invention can readily be seen. In order to maintain a high conversion temperature and sharp heating in the conversion zone, it is essential to heat the pebbles to a high temperature and flow them thru this zone at a relatively rapid rate which results in a fairly high pebble outlet temperature. It is not feasible to handle pebbles at such temperatures (1500° F.) in an elevator using ordinary cast iron buckets. Even handling pebbles at 1000° F. requires such heavy equipment as to considerably increase the cost of handling. With lower pebble temperatures, elevator equipment can be much lighter and made of considerably cheaper materials. By utilizing the air heater, lower pebble temperature without any substantial heat loss in the process is possible. Preheating air for combustion partially compensates for lowering pebble temperature in the air heater. By preheating the pebbles coming from the elevator with the hot product gases, it is possible to additionally compensate for lowering the pebble temperature prior to handling in the elevator. It is by introducing pebbles into the pebble heating zone at this higher temperature that, when coupled with preheating of the air, feed, and/or fuel, extremely high temperatures and very sharp heating in the conversion zone may be obtained. This invention makes it possible not only to attain considerably higher temperatures than are possible in conventional apparatus by conventional procedures, but makes possible much sharper heating at any given temperature, both of which advantages are extremely important in pebble heater apparatus and many processes performed therein.

I claim:

A continuous process for cracking a propane-rich light hydrocarbon stream to produce ethylene and acetylene which comprises cracking said hydrocarbon stream in a first cracking zone in contact with a gravitating compact stream of hot pebbles at a temperature of approximately 2000° F. so as to produce an ethylene-rich stream; heating a second gravitating compact stream of pebbles in a pebble heating zone to a temperature above 3000° F.; gravitating said second stream of hot pebbles directly from said heating zone through a second cracking zone passing the hot ethylene-rich stream at substantially effluent temperature directly from said first cracking zone in contact with said second stream of pebbles in said second cracking zone so as to crack said ethylene-rich stream to an acetylene-rich stream, thereby increasing the yield of acetylene by reducing decomposition thereof effected by extended reaction time at elevated temperatures; immediately rapidly water-quenching said acetylene-rich stream to a temperature in the range of 900 to 1400° F.; passing the quenched acetylene-rich stream through a pebble preheating zone positioned above said pebble heating zone in direct heat-exchange with said second pebble stream upstream of said pebble heating zone so as to further quench said acetylene-rich stream and preheat said pebbles; gravitating said second pebble stream from said second cracking zone through a pebble cooling zone in contact with a stream of air so as to cool said pebbles to a temperature below 900° F. and heat said air; passing at least a portion of said air to said pebble heating zone in admixture with fuel under combustion conditions so as to heat the pebbles therein; recycling the pebbles from said pebble cooling zone to said pebble preheating zone; and recovering the acetylene-rich effluent from said preheating zone.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
338,542	McTighe	Mar. 23, 1886
1,880,512	Spear	Oct. 4, 1932
2,389,636	Ramseyer	Nov. 27, 1945
2,399,450	Ramseyer	Apr. 30, 1946
2,405,395	Bahlke et al.	Aug. 6, 1946
2,448,922	Simpson et al.	Sept. 7, 1948